

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

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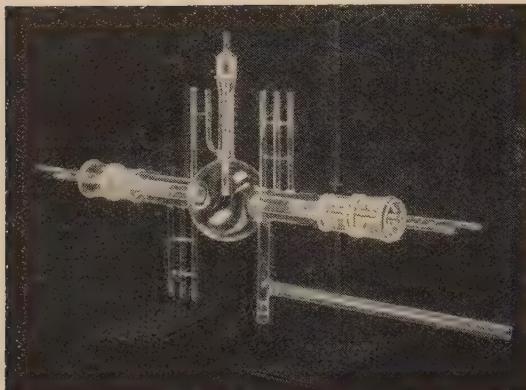
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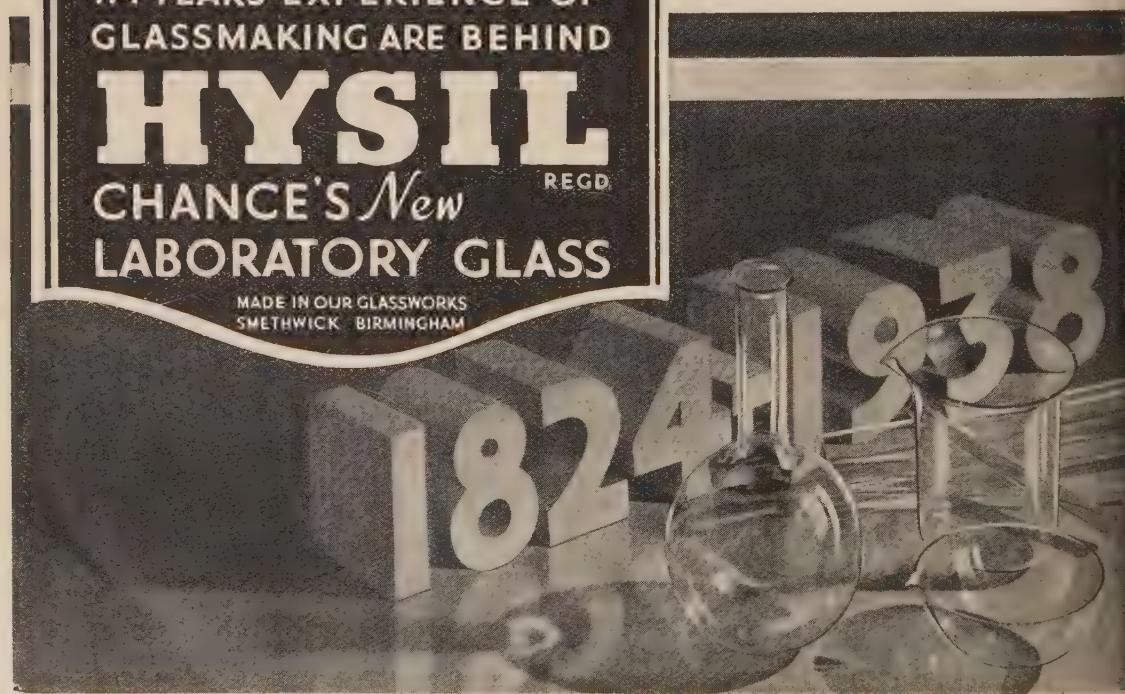
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THE STRUCTURE OF THE RETINA AND THE ROLE OF ITS VISUAL PURPLE

BY R. J. LYTHGOE, Department of Physiology, University
College, London

The Thomas Young Oration delivered 9 December 1937

WHEN Thomas Young formulated his theory of colour vision, very little was known about the structure of the retina and the anatomical paths taken by the optic nerve to the brain: nothing at all was known about the nature either of the nervous impulse or of the photochemical processes in the retina. Physiology has made considerable advances during the last few years so that it is now possible to describe with some confidence the general nature of the processes which intervene between the impact of light on the retina and the consciousness of a visual sensation. The retina contains the layer of rods and cones, and it is in these elements that the light energy initiates the nervous impulse. The rods contain the substance visual purple which is bleached by exposure to light. So far as the rods are concerned we can say that the incidence of light on their visual purple results in some bleaching of this substance and that the bleaching process initiates a nerve impulse which eventually reaches the brain. No substance comparable with visual purple has been proved to occur in the cones, but the work of Wright⁽¹⁾ indicates that the physical process taking place in these structures must be similar in nature to that taking place in the rods. The nervous impulse eventually passes to the lateral geniculate body in the mid-brain whence it is relayed by another set of nerve fibres to the occipital cortex. That this is a true picture of the general scheme could have been stated more than twenty years ago, and progress since then has been in the nature both of an elaboration of the details and of greater assurance in the direction of further research. The purpose of this lecture is to show how recent work in anatomy, chemistry and physiology has helped to fill in the details of our general scheme linking the outside physical event with the inner consciousness of sight. Nothing of what we say will be a direct contribution to the problem of colour vision, but by working out some of the details of achromatic vision, we shall have

narrowed the field of inquiry. We shall see the kind of physiological basis on which Young's theory of colour vision must rest.

Before proceeding any further we shall have to consider a most important advance in knowledge due to Schultze⁽²⁾, Parinaud^(3, 4), and v. Kries⁽⁵⁾ and known as the duality theory. This theory has in effect given us two subjects for study where only one existed before, since it has drawn a line between the factors involved in vision at low illuminations and those involved at high illuminations. Most of the physiological developments have been concerned with the achromatic vision of low illuminations, but by increasing our knowledge of this type of vision we are really defining what still has to be explained in chromatic vision at higher illuminations. It will be necessary to give some account of the anatomy of the retina on which the duality theory is based.

The retina can be divided into three distinct regions, each of which has its own functions. The rods and cones which form one of these regions are sensitive to light. The nervous impulse initiated there passes through the second region, which is composed of layers of nerve cells and their nerve fibres, before it enters a fibre of the optic nerve. These layers can be likened to a complicated network for the sorting of nerve impulses. Finally, lying on the other side of the rods and cones, and farthest away from the incident light, there is the region known as the pigment epithelium of the retina. The pigment epithelium of many animals is remarkable for its richness in xanthophyll, a carotenoid pigment which may be concerned in the formation of visual purple. Although in most animals the pigment epithelium actually contains black pigment granules, in others they are absent. When present this black layer prevents internal reflections within the eye.

In most animals it is possible to distinguish both rods and cones in the retina, but owing to the diversity of form between different species it is not always possible to decide by its shape alone whether a given element is a rod or a cone. When both types of element are present in the same retina the distinction is usually easy. The retinae of many animals appear on first sight to contain elements all of the same form and it is then often not possible to be sure whether these elements are all rods or all cones. The elements are, however, the terminal expansions of nerve cells whose nuclei form the outer nuclear layer of the retina, and although there may be great variety in the shape of the rod or of the cone amongst different animals, their nuclei differ uniformly from one another in that those of the rods are fuller of chromatin and stain more uniformly than those of the cones^(6, 7). The rods also differ from the cones in containing the substance visual purple which can be brought into aqueous solution and whose presence can be demonstrated by histological stains. The new light-sensitive substance⁽⁸⁾ recently found in chickens' retinae is present in very small quantities and it is not proved that it is present in their cones. Our ability to differentiate the two types of light-sensitive element will probably be surer when more is known about the differences in the electrical responses displayed by the retinae of various animals⁽⁹⁾. There are unexpected and striking differences between the optical properties of the retina at high and low illuminations. Pencils of light entering the pupil through its centre produce a more luminous

sensation than those entering through other points provided the illumination is high⁽¹⁰⁾. At low illuminations all rays are equally efficient⁽¹¹⁾. This phenomenon may reflect a structural difference between rods and cones.

Schultze first observed that night-hunting animals had a predominance of rods, whilst day-hunting animals had the cone type of retina. This discovery was one of the most stimulating ever made in the study of the eye, but although no one would nowadays doubt its general truth it is nevertheless not the whole truth. Who, for instance, would guess that the cat, which catches a bird so well by day, has a retina almost exclusively composed of rods, whilst the owl with a similar retina sees with such apparent difficulty by day? The physiology of vision has suffered much from dogma and we should not attempt to explain too much on Schultze's observation; it would be rash to state that the rods played no part in vision at high, and the cones no part in vision at low illuminations. There can be no doubt, however, of the general truth of Schultze's observation, and we shall see that it has been given additional force by Kolmer's observations on retinal structure and habit in the monkeys.

There is no doubt that in ourselves visual sensations differ under high and low illuminations. When the relation between any visual capacity is investigated over a wide range of illuminations it is found that below about 0.01 ft.-can. there is one relation between illumination and the visual performance in question whilst above this figure another relation will hold. There may even be well-marked qualitative differences in the visual sensation, of which the Purkinje phenomenon is a good example. At low illuminations the spectrum is colourless and the greatest luminosity is at about 502 m μ . At high illuminations not only does the spectrum acquire the quality of colour, but the wave-length of greatest luminosity moves to 550 m μ . So fundamental is the distinction, that the terms "photopic" and "scotopic" are generally used to qualify vision under high and low illuminations respectively. The essential conception of the duality theory is, however, that the cones in our retinae are the organs for photopic vision and the rods the organs for scotopic vision. Since v. Kries's time every extended observation has emphasized this distinction between the subjective aspects of scotopic and photopic vision, but the connexion between the visual sensations on the one hand and the rods and cones on the other is not so satisfactory. If the graph relating a visual performance with illumination consists of two straight lines, it is easy to label one "rods" and the other "cones", but it is another thing to prove the relationship. As we shall see later, there are difficulties in the interpretation of experiments involving the peripheral retina. In these regions, although there are relatively few cones, vision is of the photopic type⁽¹²⁾; the peripheral retina behaves in the same manner as the central retina but with diminished sensitivity. In view of these difficulties it is of importance to see how far fresh objective evidence from the retina helps in the interpretation of visual sensation. Most of the matters to be considered in this paper are connected with scotopic vision and it will be convenient to summarize modern views on this subject. In scotopic vision we can see very feeble illuminations provided we have allowed sufficient time for our eyes to become adapted. Scotopic vision is colourless vision and in general is of an undifferentiated character. It lacks exact localization and

discrimination; Parsons⁽¹²⁾ has called it "dyscritic vision". Photopic vision, on the other hand, needs relatively high light-intensities, but once in action it is remarkable for its exactitude of localization and discrimination. Furthermore, visual acuity, the perception of movement and so on, improve progressively up to very high illuminations. The acme of achievement by photopic vision is the perception of colour. Photopic vision shows some changes during adaptation to darkness but it is sometimes difficult to know how these changes should be interpreted⁽¹³⁾.

The anatomy of the nervous layers of the retina cannot be neglected if we attempt to relate scotopic and photopic vision to the rods and cones respectively. One of the most firmly held views in the physiology of sensation is that the quality of a sensation is unalterably associated with the nerve fibre connecting the end organ to the brain. However we stimulate the nerve fibre arising from a cold spot on the skin, the sensation will always be one of cold. The only respect in which a sensory nerve fibre can vary its response is in the frequency of the impulses passing up it; any one impulse is no different from any other. Experimental evidence makes it clear that the change in frequency conveys the information of a change in intensity, but that, with the rather doubtful exception of the auditory nerve impulses, this change in frequency is associated with nothing else. All that is known about sensory nerves points to the conclusion that the chromatic sensations of photopic vision should pass to the brain along nerve paths which are different from those traversed by the nerve impulses conveying achromatic sensations. If the terms "photopic vision" and "scotopic vision" can be regarded as synonymous with "cone vision" and "rod vision", then we should expect to find separate nervous pathways for each in the retinal layer of nerve cells and nerve fibres. Ramon y Cajal believed that separate nervous pathways did exist and he described "rod bipolar" cells which were in contact with rods alone and "cone bipolar" cells which were in contact with cones alone. Presumably these rod bipolars and cone bipolars were the first sections of the separate paths of the rod and cone connexions with the brain. Polyak's recent work⁽¹⁴⁾ has failed to confirm this observation. He believes that although there are separate pathways for the impulses passing from certain cones, there are no such separate pathways for any rods. Although this evidence makes it difficult to interpret differences in the quality of sensations in terms of rods and cones, it does not affect the interpretation of other properties of vision in these terms. Let us suppose we have a rod and a cone each attached to the same fibre of the optic nerve. The frequency of the impulses arising from the rods by monochromatic illumination will depend on the light absorbed by the visual purple in the rods. We should expect the greatest frequency of nerve impulses to arise from a wave-length of $502 \text{ m}\mu$. Monochromatic illumination of greater energy would stimulate the cones, and assuming that the response of the rods was swamped, the frequency of impulses would now be determined by the photochemical reactions of the cones and the greatest response would be at a wave-length of $550 \text{ m}\mu$. The corresponding shift in the electrical response has been demonstrated by Granit and Wrede⁽¹⁵⁾. Our difficulty would lie in explaining why the rod gave rise to an achromatic sensation whilst the cone gave rise to a chromatic sensation.

There is another important capacity of the eye which has an obvious anatomical basis. I refer to its resolving power or the closely-related function of visual acuity. It is sometimes stated that each cone is served by a fibre of the optic nerve and that the bundles of fibres from the cones pass to the cerebral cortex, where they end in something resembling a telephone switchboard. A one-to-one relation is assumed. If this is true, then the resolving power of the retina must be limited by the fineness of the cone mosaic, the response in a single nerve fibre being the same whatever part of a cone is stimulated. For resolution of two points of light it is necessary that there shall be two stimulated cones with an unstimulated intervening cone. The need for the unstimulated cone will be realized when one considers that to an observer at the switchboard there would be no difference between two images of light stimulating two neighbouring cones and one larger image stimulating the same two cones. Such then is the theoretical explanation of the resolving power of the eye for two points. It is well supported by experiment, since it is found that the images of two points of light can be resolved provided they are not closer together than about $4\text{ m}\mu$. on the retina, whereas the diameter of the cones is just over $3\text{ m}\mu$. It will be noticed that no proof has been advanced that a one-to-one relation does indeed exist in the retinal layers, and it is only recently that Polyak has demonstrated the existence of a suitable anatomical basis.

Polyak used sections of the retinae from monkeys (*Macacus rhesus* or *M. mulatta*) and from an ape (chimpanzee), the eye of the latter probably being identical with that of man. The nuclei and fibres of the nerve cells were stained by Golgi's method. He found that in the region of the fovea there are specialized types both of bipolar cell and of ganglion cell which produce the desired one-to-one relation between the cone and the optic nerve fibre. The bipolar cells send out extensions towards the pedicles of the cones, and these extensions in most parts of the retina end in arborizations which make contact with the pedicles of many cones and rods. The type of midget bipolar which is found near the fovea sends out an extension which ends in a compact bouquet resembling "the half-open flower of the dandelion", and this bouquet is usually a little smaller than the single cone pedicle with which it makes contact. The opposite extension of a midget bipolar connects with one of the specialized individual ganglion cells which are found near the fovea. From the other extreme of the ganglion cell there arises the fibre of the optic nerve, which suffers only one further relay, in the lateral geniculate body, before reaching the cerebral cortex.

Here, probably, we have the retinal basis of the resolving power of the eye. It should be emphasized, however, that the histological technique is difficult, and it is a characteristic of the method used that only a small proportion of the cells takes the stain. It is not known how many of these one-to-one relations occur; certainly not all the cones in the central retina are connected in this way, although the proportion is high. In the rest of the retina many cones can be seen to be linked together by the extension of a common bipolar cell. Furthermore, in all parts of the retina, especially in its central parts, there are horizontal cells which connect a number of cones with one another. These horizontal cells have no central connexions. Apparently there are no horizontal cells for the rods.

Having noted that, except in the central retina, the one-to-one connexion of cone to nerve fibre is rarely seen, we find that we should have anticipated it. The total number of cones in the human retina is about 6,600,000⁽¹⁶⁾, but there are only 500,000 fibres in the optic nerve⁽¹⁷⁾. Each optic nerve fibre arises from a ganglion cell, and Pütter⁽¹⁸⁾ measured the ratio of the number of visual elements to the number of these ganglion cells. This he did for a great many animals, and he came to the conclusion that retinal resolving power depends less on the size of the visual elements than on the area of retina supplied by an optic nerve fibre (Innervationskreis) or the visual angle subtended by that area. We can explain resolving power at the fovea and its immediate surroundings in terms of the cone diameter, but the fovea occupies less than 1/10,000th of the area of the whole retina, and we have said nothing about the resolving power of the remaining parts.

In spite of Polyak's work we do not yet know enough to explain the resolving power of the non-central parts of the retina in terms of rods, cones and their connexions. There is, however, another approach open to us; we can calculate the number of nerve fibres needed by different parts of the retina in order to explain the resolving power of each of those parts. Since we know that the expected number of cones is present to explain the retinal resolving power at the fovea, we also know, assuming the one-to-one relation, the density of nerve fibres arising from that region. Knowing the resolving power of another part of the retina relative to the fovea, we can calculate the density of nerve fibres arising there. In other words, we divide the retina into zones and first calculate the number of fibres which would be needed in each zone if the visual acuity were unity, the value at the fovea. Secondly we multiply this number by the square of the visual acuity at the point in question.

The simplest way to make the calculation is to imagine the eye at the centre of a hollow hemisphere whose radius is 1 m. The hemisphere is then divided into zones, the latter being demarcated by lines subtending various angles to the line of vision

Table I.

i Angle with line of vision (degrees)	ii Area of annular zone at 1 m. between angles (cm. ²)	iii Number of nerve fibres on foveal basis (ii × 1100)	iv Linear acuity relative to fovea	v Necessary number of nerve fibres (iii × iv ²)
7½	415	4·6 × 10 ⁵	0·22	22,000
10	1190	1·3 × 10 ⁶	0·17	38,000
15	1650	1·8 × 10 ⁶	0·12	26,000
20	2100	2·3 × 10 ⁶	0·08	15,000
25	2530	2·8 × 10 ⁶	0·06	10,000
30	2940	3·2 × 10 ⁶	0·05	8,000
35	3340	3·7 × 10 ⁶	0·04	6,000
40	3700	4·1 × 10 ⁶	0·035	5,000
45	4040	4·4 × 10 ⁶	0·03	4,000
50	4350	4·8 × 10 ⁶	0·025	3,000
55			0·02	[13,000]
90				Total 150,000

which we suppose to pass through a pole of the hemisphere, table i. For instance, lines making angles of 40 and 45 degrees will cut off an annular zone of the sphere whose area is 3700 cm.², column ii. The fovea can resolve detail subtending 1' of visual angle, that is to say points which are separated by 0.03 cm. at 1 m. or areas of 0.0009 cm.² at the same distance, and the retinal image of each of these areas would be served by one nerve fibre. An area of 1 cm.² at 1 m. would contain about 1100 of these smaller areas, and the corresponding image on the retina would have to be served by about 1100 nerve fibres to account for resolution. If acuity at between 40° and 50° with the line of sight were unity there would be about 4,100,000 areas resolvable (3700×1100) in the annular zone, column iii, and the image of each area on the retina would need one nerve fibre. According to Wertheim⁽¹⁹⁾ the visual acuity for linear objects at this angle is only about 0.035, column iv, that at the fovea and the number of nerve fibres necessary to cover the area will be $4,100,000 \times (0.035)^2$, i.e. about 5000, column v. Proceeding in this way we can find the total number of nerve fibres necessary to explain the visual acuity at all points on the retina. Owing to the very rapid change of visual acuity in the region round the fovea it would be desirable to exclude this region from our calculation. Fortunately this is possible since we can calculate⁽²⁰⁾ that the central area of the retina subtending about $7\frac{1}{2}^{\circ}$ in all directions with the line of fixation, is served by about 110,000 fibres of the optic nerve, leaving 390,000 fibres to serve the rest of the retina.

According to my calculations, using Wertheim's figures for peripheral visual acuity, about 150,000 fibres are needed to explain visual acuity between $7\frac{1}{2}^{\circ}$ and 90°. With Fick's⁽²¹⁾ figures the number of fibres is under 100,000 whilst Dor's⁽²²⁾ figures give a still lower value. Owing to the fact that lack of practice and other factors are apt to lead to abnormally low values in judgments by the peripheral retina, the largest value is probably the best.

At the fovea and in the surrounding rod-free area visual acuity is certainly served by the cones alone for the simple reason that there are no rods present. For argument's sake let us assume that in photopic vision the cones alone serve visual acuity in the rest of the retina. There are about 600,000 cones in the central retina (up to $7\frac{1}{2}^{\circ}$), and if our assumption is true the 6,000,000 cones in the non-central retina must be served by 150,000 nerve fibres, that is to say there must be 40 cones to one nerve fibre. The 110,000,000 rods must be served by the remaining 240,000 fibres, that is to say there must be over 400 rods to one nerve fibre! This result is surprising and contrary to accepted teaching. Even if all the 500,000 fibres in the optic nerve were connected exclusively to the 110,000,000 or so rods there would still be more than 200 rods to one fibre. Actually the number of elements to each fibre is greater than the calculated value because of the overlap in distribution of the fibres. Furthermore, it is assumed that all fibres have the same function whereas the observable differences in diameter probably indicate that there are differences. The actual variation in size does not appear to have been worked out carefully for the human optic nerve, but in the frog it is considerable⁽²³⁾.

The calculation of the number of nerve fibres necessary to explain visual acuity for the whole of the external field of vision does not depend on any knowledge of

the size of the eye. All we need to know is the visual acuity for all points of the outside world and we can calculate the necessary number of nerve fibres. It follows that knowing the diameter of the optic nerve, we can form an approximate idea of an animal's visual acuity. If the diameter of the mouse's optic nerve were greater than that of the elephant, then the mouse would have the better visual acuity provided it had no refractive error.

The diameter of a rod is less than that of a cone, and since visual acuity cannot demand such a fine retinal mosaic it is difficult to see why the rods need be so small. The answer to many problems of the eye lies in comparative morphology and we will therefore consider the eye of the conger whose retinal elements are very different from our own. The conger has a retina almost exclusively composed of rods⁽²⁴⁾. Its optic nerve contains about 10,000 fibres⁽²⁵⁾ of varying diameter. The retina of a small conger has an area of about 64 mm², and assuming that the nerve fibres are evenly distributed over the whole surface, the retinal area served by one fibre will be a circle whose diameter is about 90 m μ . The diameter of one retinal rod in the conger is about 2 m μ . and in the circle there will be about 1600 rods to one nerve fibre, compared with about 400 in our own. Using as a basis the area of conger retina served by one nerve fibre it is possible to calculate the resolving power of the conger's eye, and we find that the smallest detail visible to the animal must subtend an angle of 1·6° compared with 1' in our own eyes at the fovea and about 25' in the mid-periphery.

The conger therefore has a large number of fine elongated elements in its retina and yet its ability to see fine detail must be poor. Why then does it need so many fine elements? It is found, in general, that amongst sea fishes the deeper the habitat the fewer the cones and more numerous and finer the retinal rods. Arey⁽²⁶⁾ explains this change by saying that it provides the animal with an improved visual acuity, but unless there is a corresponding increase in the number of nerve fibres, this cannot be the true explanation. My own belief is that the increasing fineness of the rods with depth of habitat leads to an increase in the carrying capacity of the retina for visual purple, the latter substance being adsorbed on the surfaces of the rods. In order to substantiate this statement it will be necessary to say something about visual purple.

Visual purple is a coloured substance found in the outer limbs of the rods and, so far as one knows, in no other retinal structure. It loses its colour on exposure to light, and provided it is in a healthy living retina, the colour is reformed in the dark^(27, 28). If the retina is placed in bile salts or in one of a number of other reagents which we will mention later, the visual purple is liberated into solution. When suitably purified the solution is red in colour with a bluish tinge when dilute. The colour bleaches in a few seconds in daylight. In solution there is only a small regeneration of colour in the dark.

Visual purple if not a protein itself is very closely associated with one. Its colour is destroyed by warming, by reagents such as ether and alcohol, and by strong acids and alkalis: its resistance to heat is increased by the addition of sodium chloride, and it is precipitated by full saturation with sodium sulphate at 30° C.

Its molecular weight is probably about 100,000 as determined by the ultracentrifuge⁽²⁹⁾. Diffusion methods suggest a molecular weight which is a submultiple of 810,000⁽³⁰⁾. All these properties suggest the protein nature of the substance. Other properties, however, do not appear at first sight to bear out this view. Visual purple is not destroyed by tryptic digestion, whereas it is by lipase. In addition it is not destroyed by weak potassium alum solutions or by weak formalin.

There is little doubt that the process of dark-adaptation is due to the reformation of visual purple in the eye after it has been bleached in the light. Man and animals suffering from a deficiency of vitamin A adapt to darkness more slowly than normal⁽³¹⁾, and it has been shown^(32, 33) that such animals do not regenerate their visual purple so well as normal animals. The retinae of very many birds and fishes and amphibiae have been shown by Lönnberg⁽³⁴⁾ and Wald⁽³⁵⁾ to contain large quantities of xanthophyll. In the course of my purification of visual purple from *Rana esculenta* I obtained a yellow substance which Prof. Heilbron has kindly analysed and found to be xanthophyll. From the method used to obtain it, it is clearly either in the rods and cones, or in the pigment epithelium. If it is from the latter, as seems most likely, it must lie anatomically between the visual purple and the choroidal blood supply. The retina is also said to contain vitamin A⁽³⁵⁾. Wald has confirmed and extended these observations and has also described a new carotenoid substance, retinene. These and other observations leave little doubt that carotenes play an essential role in the formation of visual purple, and it is probable that one of these substances is an integral part of the visual purple molecule^(36, 35, 34, 37). Under certain conditions Wald finds that all three substances, namely, xanthophyll, retinene and vitamin A, are present in the retina simultaneously, but visual purple solutions contain only retinene. Wald has elaborated a hypothesis explaining the relation of these substances to the bleaching and reformation of visual purple. It should be pointed out, however, that the chemical facts are not yet firmly established⁽³⁸⁾.

Visual purple can be liberated from the rods by most of the means used to liberate haemoglobin from red blood corpuscles, but whereas mechanical injury, thawing and freezing, and distilled water will haemolyse the corpuscles, they liberate very little visual purple from the rods. In order to obtain a satisfactory yield of visual purple Tansley⁽³³⁾ found it necessary in general to use what is known as a stromalytic agent, that is to say, one which can break up the envelope of the red blood cell and can presumably break up the envelope of the rod. Even so it is necessary to use a high concentration of the stromalytic agent in order to liberate the visual purple. A large number of such agents has been used, bile salts, bile acids⁽²⁷⁾, saponin and digitonin⁽³³⁾, and panaxtoxin⁽³⁹⁾. I have found that lysolecithin, the phosphatide prepared from cobra venom, will liberate visual purple in concentrations of 1 in 10,000. A concentration of 1 in 100,000 will haemolyse the red blood cells of a sheep⁽⁴⁰⁾.

The action of weakly alkaline solutions on the rods is interesting. In general such solutions cause a complete disintegration of tissues, and their action on the rods is no exception. I find that a M./20 buffer solution of pH 10 will completely

disintegrate the cell structure of a suspension of rods, leaving only a mucoid mass in the test tube, but the visual purple will have passed into solution. The use of bile salts in addition to alkalis⁽⁴¹⁾ is unnecessary. Sometimes after the use of liquid air as an extractive, it is found that the visual purple centrifuges down after about 15 minutes at 4000 r.p.m. Such solutions are always slightly opalescent and on the acid side of neutrality. If, however, the solution is made alkaline, the opalescence disappears and the visual purple no longer sediments in the centrifuge. The interpretation I place on this observation is that the visual purple was originally adsorbed on the cell debris and that both sedimented together. When, however, the cell debris was disintegrated by alkali, the visual purple passed into true solution. Visual purple is easily adsorbed on alumina and animal charcoal without any demonstrable change in its absorption properties. In connexion with methods of preparation it may also be of interest to notice that visual purple is liberated from the rods by the negatively charged long-chain paraffin salt, palmityl sulphonic acid (sodium salt), which, if our interpretation is correct, competes with the visual purple for its place on the cell membrane. Visual purple solutions cannot be prepared by the use of cetyl pyridinium chloride, a similar but positively charged long-chain paraffin salt, but this substance acts as a very powerful haemolytic agent. The long-chain salts were given to me by the kindness of Dr G. S. Hartley.

On the whole the evidence suggests that visual purple is adsorbed on the rod envelope, but this can be regarded as little more than a suggestion. If true, it would give a reasonable explanation of the fact that deep-sea fishes, which live in very feeble illuminations, have a large number of fine rods.

It is not difficult to see that the deep-sea fish must rely relatively more on the presence of light and less on its fine localization than the surface forms. Adrian has shown that within limits the optic nerve impulses are identical, however the light is distributed in time and space on the retina. All that matters is that the product of illumination, area, and duration of flash should be kept constant. If many rods are served by one nerve fibre this result is understandable. Within narrow limits, however, the same is true for human foveal vision, namely that for a flash of light just to become visible it is necessary for the total quantity of light to be kept constant. At first sight this is difficult to explain when we remember that at the fovea there is a one-to-one relation of cone to nerve fibre. It has been shown by Polyak, however, that horizontal cells connecting the cones are present in all parts of the retina. These fibres bring small groups of cones into relation with one another in the central retina and produce interrelation of cones over a wider area in the peripheral retina. This is the probable anatomical basis of the integration of cone stimuli. No such horizontal cells were found to make contact with the rods, and so we must assume that the anatomical basis of the integration of rod stimuli lies in the ultimate concentration of many rods on one nerve fibre. In the conger retina it can be seen that the number of outer nuclei is very large, each cell to which the nucleus belongs also bearing one rod. There are far fewer bipolar cells, and this indicates that each of the latter is in connexion with many of the cells of the rods and cones. There is a still further reduction in the number of ganglion cells,

indicating a further concentration. A single optic nerve fibre arises from each ganglion cell and passes centrally. It is not known whether there is any further concentration in the lateral geniculate body.

One of the best pieces of evidence linking the rods and their visual purple with vision at low illuminations is found in the striking similarity between the scotopic luminosity curve and the absorption of visual purple at different wave-lengths. The density of visual purple in the dark-adapted retina is not known, but if it were very dense then it would appear quite black and it would absorb all wave-lengths completely. The scotopic luminosity curve would then be proportional to the number of quanta in different parts of the spectrum. If the visual purple had a density of 1·0 at 520 m μ ., it would absorb 90 per cent of the incident light, whilst the densities at 435 and 595 m μ . would be about 0·13, that is to say about 10 per cent of the incident light would be absorbed. Suppose now that the concentration and therefore the density of the visual purple were increased ten times, a condition which would be produced by replacing one large rod by about 100 small ones. At 520 m μ . practically all the incident light would be absorbed, as compared with 90 per cent before. At 435 and 595 m μ . the density would be 1·3 and the visual purple would absorb about 95 per cent of these wave-lengths as compared with 10 per cent with the smaller concentration. The only considerable increase in absorption on increasing the density occurs towards the ends of the visible spectrum. One would expect from a knowledge of the absorption curve of sea water that in a clear sea only a narrow band of wave-lengths would be transmitted to the depths. This narrow band is centred around 520 m μ .⁽⁴²⁾, which coincides with the maximum absorption of visual purple for some sea-water fishes. To such a fish lying in the dimly lighted depths the great potential increase in absorption at 435 and 595 m μ . would be of no value because those wave-lengths would not be transmitted. The increased absorption would, however, be of great advantage to a fish living in muddy water or in an underground cave.

Deep-sea fishes may improve their vision in other ways, in particular by increasing the optical apertures of their eyes. It is found that of two closely related species, one will increase the aperture in this way and so achieve some vision, whilst another will have no eye, having evolved so as to depend on sense organs other than the eye.

In ourselves the process of adaptation to darkness occupies about the same time as the fading of daylight after the setting of the sun, so that we are ready for night when it comes. Many fishes and amphibia have a mechanism in their retinae which seems admirably adapted to protect the visual purple from bleaching should the animal find it necessary to come to the bright light of the surface waters. In feeble illuminations the retinal elements are so disposed that the incident light after passing through the nerve fibre layers comes first into contact with the rods and next with the cones, and finally it is absorbed by the black pigment epithelium. In higher illuminations, on the other hand, the sensitive elements change places so that the light after passing through the nerve fibres comes into contact with the cones, the organs of day vision, but it proceeds no further because the pigment

epithelium has advanced and there the light is absorbed. The rods lie behind and in the pigment and so their visual purple is not bleached even when light is shining into the eye⁽⁴³⁾. In our own eyes no such mechanism exists, useful as it would be in explaining some of the observations made on visual perception in the peripheral retina.

The tapetum is one of the most striking features of the eyes of many animals. Although there are three varieties, the commonest form is a layer of brightly coloured reflecting cells lying between the retina and the choroid. When a tapetum is present there are no heavily pigmented granules in the pigment epithelium. The presence of the tapetum is revealed very characteristically when one is motoring along a country road at night, the eyes of the animal shining brightly red or green. Its function, which at one time was uncertain, is more obvious since Kolmer's work on primates⁽⁴⁴⁾. This author found that a night-hunting form like *Nycticebus* has a retina in which rods predominate, whilst a day-hunting form like the macaque has a retina of the cone-type. The day-hunting forms have foveae for fine resolving power, but in the night-hunting forms these are absent and indeed they would be valueless in the low illuminations in which the animal is active. A tapetum could not be tolerated by a day-hunting form since it would result in considerable intra-ocular scattering of light and a lowering of the finer visual judgments. Every night-hunting Primate has a tapetum, however, and its probable function is to reflect back light which was not absorbed in its first passage through the visual purple of the rods, so making the greatest use of all the light which is available.

The remaining aspect of the economy of visual purple is its photochemistry and concerns the events between the absorption of light and the sensory impulse in the nerve fibre. Nothing is known about the way in which the bleaching of visual purple leads to a stimulation of the nerve endings. We do not know, for instance, whether stimulation occurs during the process of bleaching or by one of the products of bleaching, but recent work has widened our view of the bleaching process itself.

It is possible to measure the rate of bleaching of visual purple in monochromatic light by passing the latter through an optical cell containing the visual purple and then allowing it to fall on a photocell. As the visual purple bleaches the deflection of the galvanometer connected to the photocell increases⁽⁴⁵⁾. I do not propose to reproduce the analyses of the bleaching process but I should like to describe the final result. Owing to biochemical difficulties we do not know whether our solutions are of pure visual purple, and for that reason we do not know the value of the quantity α , the molecular extinction coefficient. From the bleaching experiments we can, however, calculate the product $\alpha\gamma$, where γ is the quantum efficiency of the reaction. This product at 505 m μ . has the value of about 9.0×10^{-17} cm.²⁽⁴⁶⁾. For all known coloured substances α is rarely greater than about 10×10^{-17} cm.² except for those which have peak absorption bands. It follows that γ cannot be much less than unity. It would be possible for the value of α to be low and the value of γ to be greater than unity, but this can be excluded by another line of argument. If γ were greater than one, it would mean that after the absorption of a quantum by the molecule of visual purple, chain reactions occur involving other molecules, and if this were so the reaction velocity would be increased by a rise in

temperature. Hecht⁽⁴⁷⁾ has shown that the rate of bleaching remains unaltered over the range 5 to 36° C. Recently we have extended the range of temperatures, and using conditions in which the mathematical treatment of the results is not invalidated by the behaviour of intermediate breakdown products, we find that the bleaching of visual purple by light is unaffected by temperature. We conclude that the quantum efficiency cannot be greater than unity, and since it is not much less, we can say provisionally that it is about unity.

So far as its photochemical properties are concerned, visual purple plays its role in the eye ideally, since with a quantum efficiency of unity each quantum absorbed will be effective in bleaching one molecule of visual purple. A quantum efficiency greater than unity, although it would produce a greater effect, might be of no advantage to the organism since chain reactions might be involved which were drawn out in time.

The general agreement between the scotopic luminosity curve and the absorption of light by visual purple at different wave-lengths has been known for many years and has attracted considerable attention. A remeasurement of the scotopic luminosity curve⁽⁴⁸⁾ revealed that the maximum of this curve was about 7 mμ. nearer the red end of the spectrum than the maximum of the absorption curve of visual purple. Dartnall and Goodeve⁽⁴⁹⁾ have shown, however, that the fit is extremely good if the luminosity curve is corrected on a basis of equal quantum and not equal energy. It is probable that the absorption of an equal number of quanta of any wave-length will lead to the bleaching of the same number of visual purple molecules and will produce the same sensation of brightness.

The electrical changes in the retina and optic nerve resulting from illumination of the eye have attracted much attention, but it is only recently with the work of Granit and his collaborators that the relation of these changes to the visual purple mechanism on the one hand and to the conscious sensation on the other hand has become at all clear. It is possible that in a few years' time we shall be able to trace the physical consequences of the impact of a weak light on the retina from the bleaching of the visual purple through the electrical changes in the retina to the impulses in the optic nerve which are finally presented to the occipital cortex. It is important to realize that the full correlation can be expected for weak light only. Granit^(50, 51) has shown that there is a good fit between the absorption curve of visual purple and the magnitude of the electrical response in the retina. Granit has also shown that certain phenomena of the critical frequency of flicker during light and dark adaptation⁽¹³⁾ are closely mirrored in the retinal potentials⁽⁵²⁾.

One of the stumbling blocks in the study of visual purple is the correct description of the bleaching process. Kühne⁽²⁷⁾ pointed out that during bleaching by light, a yellow substance (visual yellow) makes its appearance and that this in its turn becomes colourless. Whether or not visual yellow actually exists has been a much debated point, but it is now known^(53, 54, 55) that visual yellow is a substance with acid-base properties, and its detection by earlier workers depended on the hydrogen-ion concentration of their solutions. The substance was originally called "visual yellow" because it was thought to be sensitive to light and responsible for the blue-

sensation curve in colour-vision. Since this is no longer believed I prefer to call this substance "indicator yellow". Kühne said that during the bleaching of visual purple by light other colours appeared, one of which was orange. It is easy to demonstrate spectroscopically that the orange colour is due not to a mixture of visual purple and indicator yellow, but to an intermediate form which is thermally unstable. Its exact position in the scheme of bleaching is uncertain but its existence is sufficiently obvious to justify a name and the one I have proposed is "transient orange".

A solution of visual purple has a maximum absorption at $502\text{ m}\mu.$ or so and the absorption becomes progressively less as far as $400\text{ m}\mu.$ but after that it begins to rise again. It is possible that the band centred on $502\text{ m}\mu.$ belongs to the light-sensitive grouping of the molecule whilst the absorption in the ultra-violet is due in part to impurities and in part to the protein portions of the molecule which may or may not be light-sensitive. It will be clear that one cannot determine the absorption curve of the light-sensitive part of the molecule from an unbleached solution since one does not know how much the various constituents of the solution contribute to density especially in the region 400 to $500\text{ m}\mu.$ It does not help to bleach the solution with light and to redetermine the absorption curve since newly formed chromophoric groups will have made their appearance. It is probable that the problem will be solved when one of the constituents of the complex, such as indicator yellow, has been isolated and purified, and when its absorption curve has been determined. On subtracting these values from the bleached curve, one will have the absorptions of the light-stable part of the molecule and impurities, whilst on subtracting these derived values from the densities of the unbleached solution one will find the densities of the light-sensitive part of the molecule. At the moment it is possible only to guess at the densities of the light-sensitive portion⁽⁵⁵⁾.

Although the yellow products of bleaching do not appear to play any direct part in vision by being sensitive to light, it is possible that they modify vision by acting as internal filters absorbing the shorter wave-lengths. With a high illumination of the retina most of the visual purple would be bleached, and unless it was removed there would be considerable accumulations of yellow substances. This state of affairs might seriously modify the luminosity curve obtained from the rods, but before examining this possibility let us inquire more closely into the Purkinje phenomenon.

The scotopic luminosity curve measured at very low illuminations follows the absorption curve of visual purple, and there can be little doubt that the retinal rods are the percipient organs involved. The duality theory teaches that the photopic luminosity curve is mediated by the cones. Since at an angle of 18° in the peripheral retina there are about 30 rods to 1 cone⁽¹⁶⁾ we might expect the luminosity curve to be of the scotopic type or at least to show some traces of its rod parentage. As Parsons⁽¹²⁾ says (p. 177): "One of the greatest difficulties, hitherto unsurmounted, of the duality theory is the behaviour of the periphery of the field of vision. There is overwhelming proof, derived from peripheral luminosity curves, minimal field and minimal time luminosity curves, that peripheral vision behaves in exactly the same manner as central vision, but with diminished sensitivity." In the perception

of flicker at high illuminations the peripheral retina also behaves like the central retina but with decreased sensitivity⁽⁵⁶⁾ provided large areas are not used⁽¹³⁾.

The scotopic luminosity curve has a maximum at about 502 m μ ., but if the determination is made at increasing illuminations the maximum of the curve moves slowly to about 550 m μ . when corrected on the quantum basis. We might say that during the increase in illumination the cones are stimulated more and more, and for that reason their characteristics assert themselves at the expense of the rods. In view of the difficulties encountered in the peripheral retina it might be profitable to ask whether the known properties of visual purple and its breakdown products could play any part in the Purkinje phenomenon.

At very low illuminations the luminosity curve will fit the curve for the quantity of light absorbed by a weak solution of visual purple at different wave-lengths. As the illumination of the retina is raised, so also will the breakdown of visual purple be increased. If the yellow products of bleaching were not immediately removed from the rods they would function as yellow internal filters and under certain conditions would protect the visual purple from the action of the shorter wave-lengths, so shifting the maximum absorption of light towards the longer wave-lengths. Holm⁽⁵⁷⁾ believed that the yellow products of bleaching were produced in larger amounts at high illuminations and acted as protective filters to the visual purple. Walls and Judd⁽⁵⁸⁾ have found yellow substances in the eye tissues of many animals and believe them to be protective. If the yellow products of bleaching are protective, it must be a protection which is selective for the near ultra-violet and the shorter visible wave-lengths. If the yellow products of bleaching were removed only slowly, their concentration would increase as the illumination of the retina was raised, but the concentration of visual purple would decrease and if the optical densities were not too low, there would be a progressive shift in the luminosity curve. This process could not go on indefinitely because the wave-length of maximum luminosity would pass farther and farther towards the red end of the spectrum whereas we know that it does not pass beyond about 550 m μ . One would have to assume that above certain illuminations an equilibrium is reached between the breakdown of visual purple, the removal of the yellow products and reformation of visual purple.

The published absorption curves of visual purple are accurate enough for our purpose, but the hydrogen-ion concentration of the retina is rather doubtful, and since indicator yellow varies in colour with pH it is difficult to know which values to use for the density of this substance.

In addition it is possible that the pH of the retina is lowered on illumination, and this presents a further difficulty. In the calculation which follows I have assumed a pH value for the retina of 6.5 and have used my own absorption curve for indicator yellow⁽⁵⁵⁾.

Let us assume that at a certain high illumination the concentration c' of indicator yellow is 100 times that c of visual purple. If the extinction coefficients of the visual purple and of the indicator yellow are α and α' respectively and l is the length of the rod, then the optical density of the visual purple will be αcl and that of the indicator

yellow will be $\alpha'c'l$ or $100\alpha'cl$. Of the total light absorbed at any one wave-length, visual purple will absorb

$$\frac{\alpha cl}{\alpha'c'l + \alpha cl}, \text{ or } \frac{\alpha}{100\alpha' + \alpha}.$$

If the incident light is I_0 , then the total absorbed light is given by

$$I_0(1 - 10^{-\alpha cl - \alpha'c'l})$$

and the light absorbed by the visual purple alone is given by the expression

$$\frac{\alpha I_0}{100\alpha' + \alpha}(1 - 10^{-\alpha cl - \alpha'c'l}).$$

If we express I_0 in quanta and consider an equal-quanta spectrum, then we can easily calculate the value of the expression at every wave-length. The values so obtained will give the number of quanta absorbed by visual purple at each wavelength and probably the values for the luminosity curve.

If the retinal absorption is very small the light absorbed by the visual purple is

$$\frac{\alpha I_0}{100\alpha' + \alpha}(\alpha cl + \alpha'c'l) = I_0 \alpha cl,$$

that is to say it is proportional to the density of the visual purple and is independent of the presence of indicator yellow. If, on the other hand, the retinal density is very high, then the light absorbed by the visual purple is

$$\frac{\alpha I_0}{100\alpha' + \alpha}$$

and the effect of the indicator yellow will be considerable. It is probable that neither of these conditions obtains in the retina and for the sake of an example we will assume that the density αcl of the visual purple at 502 m μ . is 0.02 . The densities at other wave-lengths are taken from the absorption curve of visual purple^(ss) and are given in column ii in table 2. The densities of indicator yellow at 100 times the

Table 2.

i Wave-length (m μ)	ii D_{VP} ($\times 100$)	iii D_{IY} ($\times 10$)	iv I_t on the assumption $I_0 = 100$	v Radiation absorbed by visual purple
420	0.40	9.0	12.5	0.39
440	0.85	6.8	20.5	0.98
460	1.34	5.1	30.0	1.80
480	1.76	3.6	41.9	2.70
490	1.92	3.0	47.9	3.14
497	1.98	2.5	53.7	3.40
502	2.00	2.3	56.2	3.50
510	1.94	1.9	61.7	3.55
520	1.80	1.5	67.9	3.43
530	1.56	1.1	74.8	3.12
540	1.24	0.8	80.8	2.57
560	0.62	0.4	89.9	1.36
580	0.22	0.1	97.2	0.50

concentration of the visual purple can be calculated from the graph given in the same paper⁽⁵⁵⁾, and at 502 m μ . the density will be about 0·230 at a pH of 6·5. Densities at other wave-lengths are given in column iii. Assuming that in a given time the radiation at each wave-length is 100 quanta one can calculate the radiation transmitted by the retina, column iv, from which one can calculate the light absorbed by the visual purple alone. These figures are given in column v. It will be seen that the greatest amount of light is absorbed no longer at 502 m μ . but nearer 510 m μ ., and it is at the latter wave-length where we would expect the spectrum to be most luminous. By assuming that transient orange with its much more prominent short-wave absorption is present in large quantities in the retina and by assuming very low concentrations of visual purple, endless possibilities are offered to a skilled computer. It should not be difficult to force the wave-length of maximum absorption as far as 550 m μ .

It seems improbable to me that yellow breakdown products are present in sufficient concentrations to produce more than a small shift in maximum luminosity. There is also some evidence to show that at least two different photochemical substances are simultaneously present in the retina. König found from the measurement of luminosity curves at various levels of illumination that although there was a gradual shift of the wave-length of maximum luminosity, the luminosity curves at intermediate illuminations were not smooth curves. There was plain evidence that two processes were contributing to the final brightness and for simplicity we will say that both the rods and the cones were active at these intermediate illuminations each adding a contribution to the final luminosity. At illuminations just above those for pure rod vision there was a bulge on the luminosity curve towards the longer wave-lengths, presumably due to the cones, whilst at higher illuminations the curve appeared to be of the all-cone type except for a bulge on the short-wave side. The curves for retinal potentials are equally striking and show the influence of cone vision at illuminations very little higher than the smallest which will produce any electrical response at all⁽⁵⁰⁾.

Disappointing though it is, we are forced to admit that we cannot find a role for visual purple in vision at high illuminations. What evidence there is indicates that the visual purple is present and must be undergoing continuous bleaching in the living eye under high illuminations, but vision shows no scotopic components under these conditions. Furthermore, even though the cones are numerically far inferior to the rods in the peripheral retina, the responses of these regions are nevertheless of the pure photopic type. Our conclusions must be that visual phenomena are interpretable under conditions of scotopic vision but that we are as far as ever from finding a material basis for phenomena of photopic vision and the mechanism of colour vision.

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THE FUNDAMENTAL UNIT OF ELECTRIC CHARGE

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ABSTRACT. A generalization of the uncertainty relationships for the case in which an electromagnetic field is present is developed. It is further shown that the atomicity of electric charge is a consequence of the integral relationships which are a feature of the quantum theory.

IT is well known that the equations of motion of a charged particle in an electromagnetic field can be expressed in the same form as those of a geodesic when we replace the old generalized momentum, \mathbf{p} , by a new momentum

$$\mathbf{\Pi} = \mathbf{p} + \frac{e}{c} \mathbf{\Phi},$$

in which $\mathbf{\Phi}$ is the electromagnetic vector potential and e is the charge on the particle⁽¹⁾. They do not however represent a geodesic in the space-time continuum—except when $\mathbf{\Pi} = \mathbf{p}$ —and hence Kaluza⁽²⁾ added a further dimension to that of space-time, thus constructing a continuum in which the paths of charged as well as those of uncharged particles were geodesics. This more extended momentum, $\mathbf{\Pi}$, was introduced into the familiar conditions of the older quantum theory. Thus the relations

$$\oint p_m dq_m = nh, \quad (m = 1, 2 \text{ or } 3)$$

which could only be applied in the absence of a magnetic field, became⁽¹⁾

$$\oint \Pi_m dq_m = nh \quad(1).$$

The importance of this modification is evident in its application to the Zeeman effect. Its importance in the new quantum dynamics has been emphasized by Gordon. It will be remembered that in Schroedinger's theory the momentum component p_m is replaced by the operator

$$\frac{\hbar}{2\pi i} \frac{\partial}{\partial q_m}$$

in Hamilton's equation. Gordon pointed out that in the more general case it is Π_m which should be replaced by this operator.

In other words p_m must be replaced by

$$\left(\frac{h}{2\pi i} \frac{\partial}{\partial q_m} - \frac{e}{c} \phi_m \right).$$

Dirac in his electron theory substitutes

$$\left(\mathbf{p} + \frac{e}{c} \boldsymbol{\Phi} \right)$$

for \mathbf{p} ; in this case e denotes the charge of the electron. A feature of the later quantum dynamical theory is the uncertainty relationships

$$\Delta p_m \Delta q_m \sim h, \quad \Delta W \Delta t \sim h \quad \dots \dots (2),$$

in which the values of m are 1, 2 or 3 and, if we use the notation of the theory of relativity, we can write equations (2) in the single statement

$$\Delta p_m \cdot \Delta x_m \sim h \quad \dots \dots (3),$$

in which m has the values 1, 2, 3 or 4.

When an electromagnetic field exists equation (3) must, it is clear, be generalized to take the form

$$\Delta \Pi_m \cdot \Delta x_m \sim h \quad \dots \dots (4).$$

The fourth of these, for example, is identical with

$$\Delta (mc^2 + eV) \Delta t \sim h \quad \dots \dots (5),$$

where V is the ordinary scalar potential, $(mc^2 + eV)$ denoting the total energy W of the particle.

Kaluza replaced the square of the interval ds^2 , equal to $g_{mn} dx^m dx^n$, which is characteristic of the Riemannian geometry of the space-time continuum, by $d\sigma^2$, equal to $\gamma_{\mu\nu} dx^\mu dx^\nu$. The coefficients $\gamma_{\mu\nu}$ are of course different from the g_{mn} and they are more numerous. We require to note the values of those coefficients only in which the subscript 5 occurs:

$$\gamma_{m5} = \gamma_{5m} = \gamma_{55} \alpha \phi_m \quad \dots \dots (6),$$

while the contravariant ones are:

$$\gamma^{m5} = \gamma^{5m} = -\alpha \phi^m \quad \dots \dots (7),$$

α being a new constant characteristic of Kaluza's theory.

In Einstein's relativity the momentum component p_m , of a particle, may be written

$$p_m = m_0 g_{mn} \frac{dx^n}{d\tau},$$

in which m_0 is the rest mass of the particle and $d\tau$ is the element of proper time defined by

$$ds^2 = -c^2 d\tau^2.$$

The extended momentum Π_m is expressed by

$$\Pi_m = m_0 \gamma_{mv} \frac{dx^\nu}{d\tau} \quad \dots \dots (8).$$

The familiar summation is implied in both definitions; but while the summation with respect to n in the former extends from 1 to 4, the summation with respect to v in the latter extends from 1 to 5. In Kaluza's theory we have of course a fifth component

$$\Pi_5 = m_0 \gamma_{5v} \frac{dx^v}{d\tau} \quad \dots\dots(9),$$

and when we identify this component with charge divided by αc , or $q/\alpha c$, the equations of motion of the charged particle become those of a geodesic⁽³⁾. It may be noted that the conservation of the momentum $\mathbf{\Pi}$ includes the principle of momentum in its narrower sense as well as that of mass, energy and charge.

The incompleteness of the uncertainty relationships (4) is now easily removed, for the appearance of $q/\alpha c$ as a momentum with the implied inclusion of the conservation of charge in a generalized principle of conservation of momentum suggests and indeed requires the further uncertainty relationship:

$$\Delta \Pi_5 \Delta x^5 \sim h \quad \dots\dots(10).$$

Now we can learn nothing about x^5 by any measurement and therefore the uncertainty, Δx^5 , is infinite and $\Delta \Pi_5$ consequently zero. This simply means that under all circumstances there is no limit to the precision with which Π_5 , and therefore also q , can be known.

The co-ordinate x^5 occurs in a very restricted way in the theory of Kaluza and Klein. It has in fact the character of a cyclic co-ordinate. The corresponding momentum Π_5 is constant and enters the wave equation through the factor

$$e^{(2\pi i \Pi_5 / \hbar) x^5}.$$

We may compare the co-ordinate x^5 with the co-ordinate θ of a rigid body rotating about a fixed axis under no forces, and Π_5 with the corresponding momentum, p_θ . It is well known⁽⁴⁾ that

$$p_\theta = nh/2\pi,$$

a result which can be derived from the old quantum condition

$$\oint p_\theta d\theta = nh \quad \dots\dots(11).$$

The corresponding condition involving Π_5 and x^5 is

$$\oint \Pi_5 dx^5 = nh \quad \dots\dots(12)$$

or

$$\Pi_5 l_0 = nh,$$

where l_0 is some fundamental periodic length of x^5 . Therefore

$$\frac{q}{\alpha c} l_0 = nh$$

or

$$q = nh\alpha c/l_0 \quad \dots\dots(13).$$

Hence a charge is made up of integral multiples of a unit e which is equal to $\alpha ch/l_0$.

Thus the atomicity of charge is the outcome of the integral relationships which have been an essential and characteristic feature of the quantum theory since the

constant h was introduced by Planck. The application of Kaluza's theory made by Klein in his description of the quantum theory suggests that l_0 may be conveniently replaced by h/m_0c . This means that we replace the fundamental constant l_0 by another, m_0 , of the dimensions of mass. We now obtain from equation (13) the result that the ultimate unit of electric charge may be expressed by

$$e = \alpha m_0 c^2 \quad \dots \dots (14).$$

If the value of α thus obtained be introduced into Kaluza's theory, we find that the geodesic represents the motion of a charge e associated with mass m_0 in an electromagnetic field. Thus m_0 naturally takes the place it would occupy in the equation, if it were regarded as the electromagnetic mass of the charge e . This is the justification, according to our view, of the term "mass of the charge" for m_0 . But it is free of those limitations which are implied in the derivation of this mass in the usual way by endowing the charge with a structure. Thus l_0 becomes identical with the familiar fundamental length h/m_0c described as the Compton wave-length.

The other fundamental length close to that described in the classical theory as the radius of the electron arises at once from equation (14) since we have

$$\alpha e = e^2/m_0 c^2.$$

Although it does not contain h , it emerges from the principles of the quantum theory. On this point we are in disagreement with Born, who holds that the problem of introducing the so-called radius of the electron, and the difficulties associated with electron-structure have nothing to do with the quantum theory⁽⁵⁾. Equation (14) makes it possible to describe the path of the charge e by means of a null geodesic. We may therefore regard an electron, a positron (which is simply an electron with its fifth component of momentum reversed) and a photon as different aspects of the same thing.

We have to account for the fact that the electron appears to possess a property which has hitherto been described by giving it a radius. The question is, what is the meaning of this from our point of view? It has been shown that both the equation of Schrödinger and that of Dirac⁽⁶⁾, when applied to an electron in an electromagnetic field, can be regarded as gauging equations. That is to say, they suggest that a particular form of gauging is adapted to the description of the physical world.

The form is a modification of that originally suggested by Weyl and generalized by Eddington in order to include electromagnetic phenomena within the theory of relativity. The modification has the advantage that it gives to Weyl's theory the physical content of which it was deprived by his own standpoint with regard to it.

With this view of the nature of the quantum equations in mind, it has recently been shown⁽⁷⁾ that it is impossible to regard two electric charges e as lying closer together than a distance of the order $e^2/m_0 c^2$, which by equation (14) is the same as αe .

It would thus appear that any charge e can be regarded as surrounded by a region of linear dimensions of this order which may be regarded as the exclusive property of the charge, and to distinguish between points lying within this region

would have no meaning. The region is for physics what the point singularity is for mathematics⁽⁸⁾.

This metrical argument introduces the electron radius as a limitation imposed on measurement by a peculiarity of space-time, or at least of our method of space-time description. It has been shown from the same point of view that another limitation exists with regard to measurement along the track of the geodesic which represents the path of the electron. The limitation is that it is not possible to distinguish two points on the path which lie closer together than the length h/m_0c ; this follows from the fact that the geodesic is a null geodesic and that x^5 has only the values nh/m_0c .

Whether these considerations actually justify us in concluding that these two fundamental lengths are of the nature of minima in the physical world or not, is uncertain. But we can at least say that it would be surprising if, with our present methods of description, lengths less than these were to be discovered as significant in any observation.

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OXIDE-COATED CATHODES: I. PARTICLE-SIZE AND THERMIONIC EMISSION

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*Communicated by Dr C. C. Paterson, 11 August 1937.
Read in title 25 February 1938*

ABSTRACT. The emission from an oxide cathode increases as the particle-size of the oxide decreases. It is shown that the smaller particles give a more uniform emitting surface and increase the ratio of emitting to non-emitting areas. The size of the oxide particles is determined by the method of preparation of the carbonates. The carbonate particles generally undergo no change of size in the process of conversion to the oxide state, but the method of preparation can cause particle-growth during conversion.

§ I. INTRODUCTION

THE modern high-efficiency oxide cathode consists of barium and strontium oxides applied to a suitable core metal. The cathode is generally prepared by coating the core metal with a barium-strontium carbonate which is decomposed to the oxide by subsequent heating in vacuo. In previous papers^(1, 2) we have shown that the maximum thermionic efficiency is obtained when the oxides are present as a homogeneous solid solution, whose chemical composition can vary from equal parts by weight to equal molecular proportions. A homogeneous solid solution of oxides is invariably obtained if the starting-point in the preparation of the oxides is a homogeneous double carbonate.

The results that we have obtained during recent years with such oxide cathodes have led us to believe that the thermionic efficiency of the double oxide is influenced by the method of preparation and application of the coating to the core metal. We have carried out an investigation into the effect of the method of preparation of the double carbonate on its particle-size, and the effect of the particle-size of the carbonate on the thermionic emission of the resulting oxide coating. In order to understand the results obtained, a knowledge of the physical state and appearance of the final emitting surface was necessary, and for this reason we have used an electron microscope to view the emitting oxide surface.

Although this paper is concerned mainly with the thermionic properties of oxide coatings, brief accounts of the methods of preparation of the double carbonates and the effect of the particle-size on time of decomposition to oxide have been included, because these factors play an important part in ensuring the uniform

results necessary in the successful commercial manufacture of devices using oxide cathodes.

§ 2. EXPERIMENTAL DETAILS

(1) *Method of preparation of the carbonates.* The double carbonate is precipitated by the addition of an equivalent amount of alkali carbonate, such as ammonium or sodium carbonate, to a neutral solution of the nitrates, or by passing carbon dioxide gas into an alkaline nitrates solution. The particular method used has a marked effect on the particle-size of the resultant double carbonate. By varying the nature of the alkaline agent or the precipitating carbonate, we have obtained a number of carbonates with different particle-sizes.

(2) *Method of test.* (a) *Application of the coatings.* The different carbonates were all ball-milled for 24 hours in a suitable organic medium in order to form a spraying suspension. The coatings were then sprayed on to cylindrical nickel cathodes,* 35 mm. in length and of external diameter 1.5 mm., so that the coating weight was 5 mg./cm.². This corresponded to a coating thickness of 0.1 mm. and left none of the nickel core visible. The spraying conditions were fixed so that all the sprayed coatings had the same appearance. Sample cathodes were taken from each batch, the coating was removed, and the particle-size was measured under the microscope. X-ray examinations of the coatings were also made to determine their physical state and crystal structure.

(b) *Decomposition time and thermionic emission.* The sprayed coatings were assembled in simple diode valves. The anodes were of nickel mesh, cylindrical in shape, 10 mm. wide and 34 mm. long. A barium-magnesium alloy getter was used, and the diodes were pumped with a three-stage mercury-vapour pump with liquid air. The procedure was as follows. The valve was baked at 400° c. and the anode was out-gassed by high-frequency heating. The cathode was then heated at 950° c.† for 30 sec., and at 1100° c. until decomposed. The time taken for a given coating to decompose was defined as the time taken for a Pirani gauge fitted between the valve and liquid-air trap to fall to a given value of pressure. This is made clear in figure 1, which shows a typical {time, pressure} curve. The time taken for a coating to decompose is given in arbitrary units in table 2, for in practice the actual time will depend on the characteristics of the particular pump used. After decomposition, the valves were gettered and sealed off. Cathodes were then activated by drawing 100 ma. space current with the cathode at 1000° c. Emission-measurements were made after the temperature had been lowered to about 600° c. (The power supplied to the cathode was 1 w./cm.²)

(c) *X-ray analysis.* The final state of the oxide was determined by X-ray analysis, by a method described in a previous paper⁽¹⁾. Sample coated cathodes were mounted so that after treatment the cathode could be dropped into an evacuated thin-walled glass tube which was then sealed off. The apparatus is shown in figure 2.

* The percentage composition was as follows: nickel over 99.5, magnesium 0.07, iron 0.15, manganese 0.05.

† All temperatures are brightness temperatures measured at the end of each period, for the thermal emissivity of the coating changes as it decomposes, and the temperature rises at a fixed cathode voltage. The temperatures correspond to cathode wattages of 6.5 w./cm.² and 9.0 w./cm.² respectively.

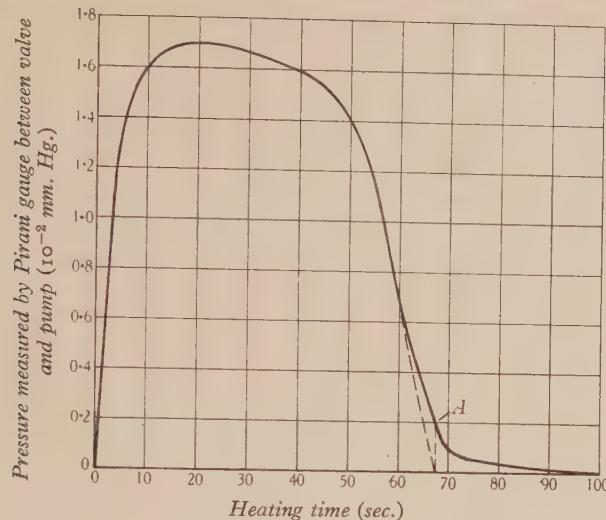


Figure 1. Typical outgassing curve for carbonate coating.

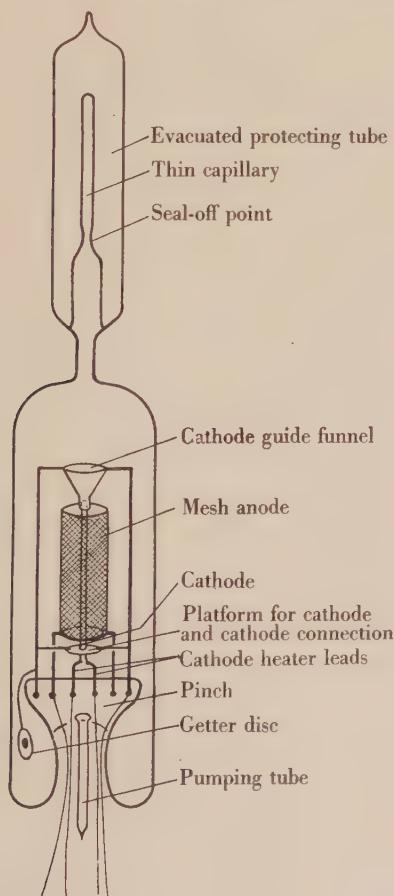


Figure 2. Apparatus for X-ray examination of oxide coating.

§ 3. APPEARANCE OF THE COATING: THE ELECTRON MICROSCOPE

An attempt was made to assess the appearance of the oxide coating after activation. Owing to the rapidity with which the coating changes to hydroxide and carbonate on exposure, it must be examined in a vacuum. The method used for X-ray examination makes this possible, but unless a marked change in appearance has taken place no information about the particle-size of the oxide is obtained. In order to examine the oxide surface in the active condition, an electron microscope was used.

A diagram of the apparatus, which is based on a microscope described by Johannson⁽³⁾, is shown in figure 3. It consists essentially of an electron immersion lens formed by small coaxial apertures in two metal diaphragms placed close together. In the figure, *A* and *B* are two circular copper-nickel plates 0·4 mm. thick, separated from each other by a steatite insulator 1·0 mm. thick. The aperture in *B* is slightly coned, being 1·0 mm. diameter at the front and 1·5 mm. diameter

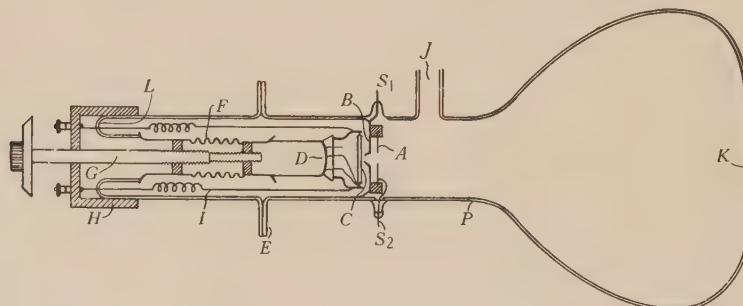


Figure 3. Electron microscope.

at the back. The two diaphragms are supported in the neck of the large bulb *P*, and constitute the electron lens. The cathode core *C* is of nickel, of rectangular cross-section 1·5 × 2·5 mm., and is 26 mm. in length. It is heated by a W-shaped heater wire, and the heater-cathode system is designed so that it makes a push fit on to the supports in the pinch *D*. This arrangement permits rapid interchange of cathodes. The pinch *D* is connected by a glass-to-metal seal to the Tombak bellows *F* and the differential screw arrangement *G*. The pinch end of the system forms a vacuum-tight seal with the main bulb at the ground-glass joint *E*, which has a very large bearing surface. The willemite screen *K*, distant 30 cm. from *A*, is sprayed on the wide portion of the bulb. The whole apparatus is evacuated through the wide bore tubing *J*, which is connected to a three-stage mercury vapour diffusion pump. The leads to the lens are taken out through the walls of the bulb at *S*₁ and *S*₂, and the bulb is internally carbonized from *S*₂ to the screen to avoid bulb charge effects. The carbon surface is connected to the high-voltage lead *S*₂. The heater and cathode leads are taken through the circular seal *L* to the cap *H*. The filament is heated by direct current, so that variable magnetic field effects are avoided. The theory of such a system is dealt with by Brüche and Scherzer⁽⁴⁾. A magnified image

of the cathode surface is thrown on to the screen at *K*. The magnification depends on the distance of object and image from the lens, and on the ratio of the voltages V_A , V_B applied to *A* and *B* respectively. V_A is approximately 4000 v., and V_B , the focusing voltage, is adjusted to be either slightly positive or slightly negative until a sharply focused image of the cathode surface is obtained on the centre of the screen. The bellows enables the distance of the cathode from the lens to be adjusted, and the cathode is usually set at 0.5 mm. from *B*. The cathode surface can be moved across the lens in either a horizontal or vertical direction by sliding the pinch end of the tube across the joint *E*. The magnification that can be obtained, consistent with sharp focusing, is about $\times 100$.

The microscope is operated in the following manner. The cathode, coated on one flat face with the required coating, is fitted to the pinch, and the ground-glass joint is made vacuum-tight with apiezon L grease. The apparatus is then evacuated, and the pump is operated throughout the time during which the microscope is in use. The cathode is de-gassed and then activated in the ordinary way by drawing space current from it to the plate *B*. The cathode-temperature is then reduced until the emission from the part opposite the aperture is saturated with V_A at about 3000 to 4000 v. This happens at about the normal operating temperature, 750° c., and the image is focused by varying V_B . The image is photographed in the ordinary way. The camera used was of an *F/4.5* double-extension quarter-plate type, orthochromatic plates were used, and the brightness of the image was such that an exposure-time of only a few seconds was necessary.

§ 4. RESULTS

In table 1 we have summarized the different methods of preparation and their effect on the size and shape of the carbonate particles. In figures 4 to 11 are shown ordinary photomicrographs of the particles. The coatings were examined after they had been removed from the sprayed cathodes. In table 2 we have recorded the effect of the particle-size of the sprayed coating on the time of decomposition and the thermionic emission. In the list of carbonates we have included a barium-strontium-calcium triple carbonate and barium-calcium double carbonate. The last two find application in the manufacture of cathodes for special devices such as high-voltage rectifiers operating at high temperatures.

(1) *Method of preparation of carbonates in relation to particle-size.* On reference to table 1, it will be seen that the following conclusions can be drawn. (a) When the carbonates contain barium and strontium (*K* carbonates), or barium, strontium and calcium (*S* carbonates), the particles have a witherite structure. Much finer particles are obtained with the sodium-carbonate method of precipitation than with the ammonium-carbonate method. The ammonium-carbonate method gives irregular aggregates with some spherulites, while the sodium-carbonate method gives mainly needle-shaped particles. (b) When the carbonates contain barium and calcium only (*R* carbonates), the particles have a calcite structure. The sodium-carbonate method of precipitation then gives a slightly larger particle than the ammonium-carbonate method. The particles are also spherulites in each case.

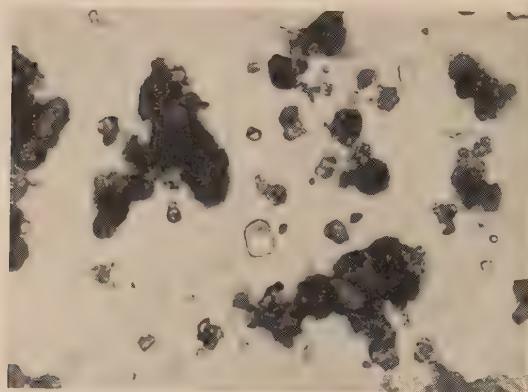
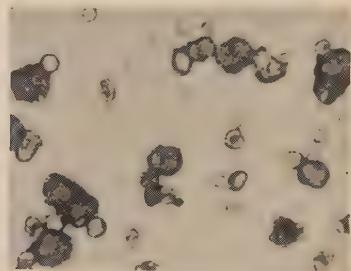
Table I. Effect of method of preparation on particle-size of carbonates

Nomenclature	Composition (parts by weight)	Method of preparation	X-ray analysis		General particle-size before milling ($\mu.$)	Particle-shape after milling	Speed of precipitant (cm. ² /min.)
			Constitution	Structure			
K_1	Ba, Sr equimolecular	$(\text{NH}_4)_2\text{CO}_3$ added to nitrates solution. Made alkaline with NH_4OH	Homogeneous double carbonate	Witherite form	50	Large aggregates; mainly spherulites	350 750
K_2	Ba, Sr equimolecular	Na_2CO_3 added to nitrates solution	Homogeneous double carbonate	Witherite form	3	Fair number of prismatic needles	350 750
K_3	Ba, Sr equimolecular	CO_2 passed into nitrates solution. Made alkaline with NH_4OH	Generally two phases very close together	Witherite form	15	Mainly spherulites	1000
K_4	Ba, Sr equimolecular	CO_2 passed into nitrates solution. Made alkaline with NaOH	Generally two phases close together	Witherite form	Less than $\frac{1}{2}$	Large number of needles	1000
S_1	Ba 56, Sr 31, Ca 13	$(\text{NH}_4)_2\text{CO}_3$ added to solution of nitrates. Made alkaline with NH_4OH	Homogeneous triple carbonate	Witherite form	100	Large crystal-line aggregates	350 750
S_2	Ba 56, Sr 31, Ca 13	Na_2CO_3 added to nitrates solution. Made alkaline with NaOH	Homogeneous triple carbonate	Witherite form	7	Fair number of needles	350 750
R_1	Ca, Ba equimolecular	$(\text{NH}_4)_2\text{CO}_3$ added to nitrates solution. Made alkaline with NH_4OH	Homogeneous double carbonate	Calcite form	3	Mainly spherulites	350 750
R_2	Ca, Ba equimolecular	Na_2CO_3 added to nitrates solution. Made alkaline with NaOH	Homogeneous double carbonate	Calcite form	10	Spherulites	350 750

* The temperature of precipitation was varied from 35 to 90° C. without any effect on particle-size.

Table 2. Data relating particle-size of carbonates with time of decomposition and thermionic emission

Carbonate	General particle-size after milling ($\mu.$)	Figure no.	Time of decomposition (arbitrary units)	Emission at 1 w./cm. ² diode (ma.)	State of final oxides	Appearance of oxide surface
K_1	50	4	100	70	Homogeneous solid solution	Unchanged
K_2	3	5	94	130	Homogeneous solid solution	Unchanged
K_3	15	6	Not tested	Not tested	—	—
K_4	< 2	7	Not tested	40	Homogeneous solid solution	Crystals had obviously grown, and coating had shrunk
S_1	100	8	94	50	Homogeneous triple oxide	Unchanged
S_2	7	9	86	140	Homogeneous triple oxide	Unchanged
R_1	3	10	81	35	Separate phases of equal strength, 80 Ca, 20 Ba; 20 Ca, 80 Ba	Unchanged
R_2	10	11	81	35	Separate phases of equal strength, 80 Ca, 20 Ba; 20 Ca, 80 Ba	Unchanged

Figure 4. K_1 carbonate.Figure 5. K_2 carbonate.Figure 6. K_3 carbonate.Figure 7. K_4 carbonate.Figure 8. S_1 carbonate.Figure 4-8. Photomicrographs of carbonate particles. ($\times 500$.)

(c) When carbon dioxide is used as the precipitating agent for barium-strontium carbonates, then very fine particles are obtained in the presence of sodium hydroxide, and the particles are mainly needle-shaped. In the presence of ammonium hydroxide the particles are larger, but still smaller than those obtained with ammonium carbonate. Again the particles are mainly spherulites.

In the case of the carbon-dioxide method the rate of precipitation is very slow, and the final product is not a truly homogeneous double carbonate. The two phases are sufficiently close together, however, to have no effect on the thermionic emissions.



Figure 9. S_2 carbonate.

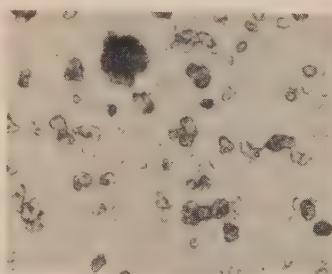


Figure 10. R_1 carbonate.

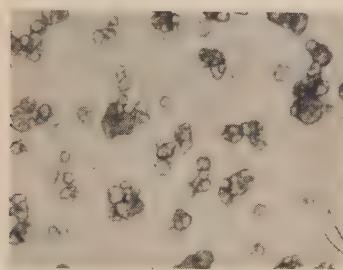


Figure 11. R_2 carbonate.

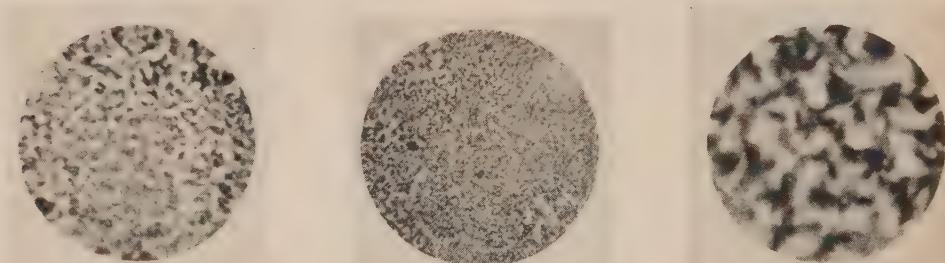
Figures 9-11. Photomicrographs of carbonate particles. ($\times 500$.)

(2) *Particle-size of carbonates in relation to decomposition time.* On reference to Table 2, the following conclusions about the effect of the particle-size of the carbonates on decomposition time and emission can be made. (a) The time of decomposition increases somewhat with increase in particle-size of the carbonate. (b) In each group of coatings a higher thermionic emission is obtained as the particle-size decreases. K_4 at first appears to be an exception, but it was apparent that the final oxide coating had shrunk during the heat treatment on the pump, and this suggested that the particles had probably grown. It may be significant that the finer particles also have the needle type of crystals.

**§ 5. PARTICLE-SIZE OF THE OXIDE IN RELATION
TO THERMIONIC EMISSION**

In figure 12 (*a*, *b*, *c*) are shown the electron photomicrographs of K_1 , K_2 and S_1 carbonates. It must be pointed out that the reproductions give no indication of the intensity of the emission, but only indicate the distribution of emission over the surface of the coating. In general, however, the emission-intensity is the same for coatings of the same composition. The size of the emitting spots (white in the figure) is of the same order as the size of the original carbonate particles in each case, and the spots represent the oxide particles on the coating surface. The electron photomicrographs indicate that the differences in thermionic emissions between different coatings can be attributed to some extent to the differences in covering power of particles of different sizes, which give rise to varying emissive areas.

The coating is about $100\mu.$ in thickness, and the particles range from 30 to $100\mu.$, so that the number of layers present can vary from 30 layers to 1 layer. (In



(*a*) K_1 carbonate sprayed coating. (*b*) K_2 carbonate sprayed coating. (*c*) S_1 sprayed coating.

Figure 12. Electron photomicrographs. Electron image. ($\times 100$.)

actual fact it can be taken that at least two layers were present in the case of the $100\mu.$ particles, for no core was visible.) Since the particles suffer little change in size in passing from the carbonate to the oxide form, it is to be expected that a fine-particle carbonate will give a much smoother surface than a coarse-particle carbonate. It is difficult to measure the actual emitting areas in the photographs, but the ratio between K_1 and K_2 is approximately 3:4. This figure makes no allowance for variations in emission-intensity over any particular particle, and may be compared with the ratio of 1:2 obtained with the diode case at a lower measuring temperature, which is of roughly the same order.

In figure 13 is shown the electron photomicrograph of K_4 coating. It is apparent that the particles are extremely large (about $70\mu.$) and that therefore the particles, originally $\frac{1}{2}\mu.$, have grown considerably in the process of decomposition to oxide. The ratio of the emitting area to that of K_1 is as 5:9, whilst the diode measurements gave 4:7, the agreement again being quite good.

The results indicate that the thermionic emission would be uniformly spread over the oxide surface if the particles were very small. In order to test this view, a

double carbonate was prepared in colloidal form, and its electron image was examined.

§ 6. COLLOIDAL CARBONATE COATING

Patai and Tomaschek^(5, 6) have described methods of preparing double carbonates of barium and strontium in colloidal form. The coating is deposited on the core by an electrophoretic method. We have prepared such a coating, and in

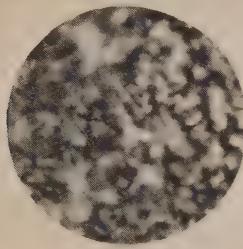


Figure 13.



Figure 14.

Figure 13. Electron photomicrograph. Electron image $\times 100$. K_4 sprayed coating.

Figure 14. Electron photomicrograph. Electron image $\times 100$. Colloidal carbonate—applied by electrophoresis.

figure 14 the electron image is shown. It will be seen that the surface is very uniform, a result that fits in with the views expressed above, for the carbonate particles are of the order of 0.1 to 0.02μ , and no growth appears to occur on decomposition. In this connexion Buzágh⁽⁷⁾, in a recent publication, indicates that there is a value of particle-size, just below the upper limit of colloid size, which gives the greatest emission-efficiency.

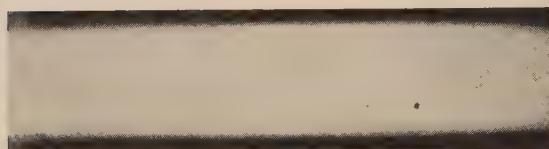
§ 7. EFFECT OF METHOD OF APPLICATION OF COATING ON THERMIONIC EMISSION

In the experiments described above a given method of spraying the coating on to the core metal was used. Now it is possible to obtain different appearances of the sprayed carbonate, ranging from a powdery appearance to an enamel-like appearance according to the degree of wetness of the spray, which can be controlled by the nature of the diluents used in the spraying suspension. In figure 15 (a, b) we show optical photomicrographs which indicate the types of surface that can be obtained. Figure 15 (a) shows the typical surface employed in the experiments already described (medium wet spray) and figure 15 (b) shows the smooth enamel-like surface that can be obtained with a very wet spray. We have carried out some experiments using a very wet method of application. The suspensions were made up with a large quantity of a diluent which was not readily volatile and it was applied by being painted on to the core metal so that it was running wet. In figure 16 are shown the electron images of K_1 , K_2 and S_1 applied by this method. It will be seen that the K_1 and K_2 images, figure 16 (a, b), are similar to those shown in figure 12 (a, b), but that the S_1 image, figure 16 (c), appears very different from that

shown in figure 12 (c). Its surface appears quite uniform, and as though it were composed of fine particles. This experiment has been repeated a number of times, and in each case a similar result was obtained. The explanation lies in the fact that S_1 differs from K_1 and K_2 in having a very wide spread in particle-size. The particle-size ranges from less than $\frac{1}{2}\mu$. to more than 120μ ., with the greater number of particles

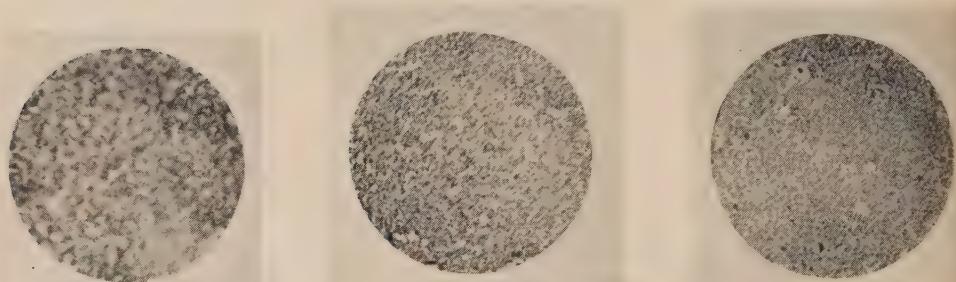


(a) Medium wet spray.



(b) Very wet spray.

Figure 15. Optical photomicrographs of sprayed coatings. ($\times 10$.)



(a) K_1 carbonate applied wet. (b) K_2 carbonate applied wet. (c) S_1 carbonate applied wet.

Figure 16. Electron photomicrographs. Electron image. ($\times 100$.)

at 100μ . A suspension of this nature settles quite rapidly, leaving the finer particles in suspension. In the spray process, where the rate of drying is quite fast, the surface is typical of the particles present in the well-agitated spraying suspension. In the paint process the rate of drying is slow, and the large particles settle rapidly leaving the fine particles in the top surface. The result is important in that it demonstrates that with a carbonate coating where the range of particle-sizes is very large, the method of application may determine to some extent the thermionic results obtained.

§ 8. INTERPRETATION OF THE ELECTRON IMAGE

The work of Brüche⁽⁴⁾ and his collaborators has shown that the electron image is a very good representation of the image that would be seen with an optical microscope. In the photographs we have shown, it has been taken that the emitting spots are images of the oxide particles in the coating surface. It is interesting, however, to inquire into the meaning of the dark patches. Figure 17 shows how a section through the coating would appear. Particles 1 and 3 are on the surface and particles 2 and 4 just below it. Three possible explanations can be suggested for the dark



Figure 17. Diagram of section through coating. Core metal.

patches: (1) They may represent gaps in the coating extending down to the relatively non-emitting core, although this is hardly likely to be the case when the particles are of the order of 3μ . in size. (2) They may be images of particles of normal emitting power, which appear non-emitting because of the space-charge effect in the hollows. (3) They may represent particles below the surface which are in fact relatively non-emitting. It is important to know the true explanation, for it may throw some light on the question of the mechanism of the emission. We have devised a series of experiments which deal with the points raised, and we hope to publish the results in the near future.

§ 9. ACKNOWLEDGEMENTS

In conclusion we desire to tender our acknowledgements to the General Electric Company and the Marconiphone Company on whose behalf the work which has led to this publication was done.

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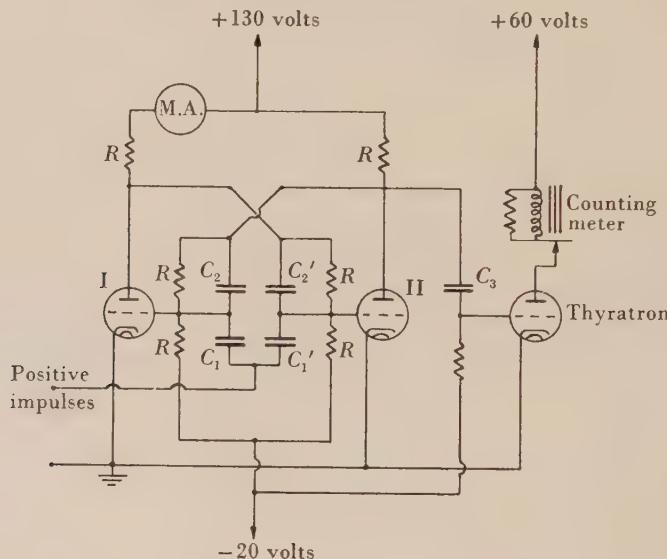
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A SIMPLE SCALE-OF-TWO COUNTER

By HANNES ALFVÉN

Communicated by Prof. M. Siegbahn 14 January 1938. Read in title 11 March 1938

IN a recent paper W. B. Lewis⁽¹⁾ has described a scale-of-two counter using hard vacuum tubes instead of thyratrons. Since about a year ago I have been using a scale-of-two counter which in certain respects is similar to that of Lewis, but as his chokes and cuprous-oxide rectifiers are not necessary in my scheme the latter may be a little simpler. A one-step scale of two of this kind has been used in re-



Valves I and II, Philips B 2038 ($\mu = 33$, $S = 3.5$ ma./v.). All resistances $R = 0.2$ M Ω ; $C_1 = C_1' = 1000$ cm.; $C_2 = C_2' = 500$ cm.; $C_3 = 1000$ cm. For high-speed counting smaller condensers are preferable.

cording cosmic rays at a rate of about 100 impulses per minute, but it can equally well be used in high-speed counting. There are no critical circuit constants, as there are for counters using oscillating valves for example. The counter has worked perfectly with no adjustments at all during several months of continuous counting, for 10^7 impulses.

The circuit is shown in the figure. Just as in Lewis's circuit there are two stable conditions, (1) Valve I is blocked and current flows through valve II; (2) Valve II is blocked and current flows through valve I.

In the first case the plate and grid voltages of the valves are approximately as follows: (I), $V_p = +65$ v., $V_g = -8$ v.; (II), $V_p = +4$ v., $V_g = +1$ v. In the second case the voltages of valve I and valve II are exchanged.

Suppose now that a positive trigger impulse with an amplitude of at least 10 v. arrives, when the counter is in condition (1). As the grid of valve II is positive the grid resistance is rather small, so that the impulse does not change the grid voltage, and consequently does not change the plate voltage of valve II very much. On the other hand, as the grid of valve I is negative the grid resistance is very large, so that the grid voltage increases considerably when the impulse arrives. When the grid voltage reaches about -2 v. plate current starts. Because of that the plate voltage of valve I drops very much, which gives a strong negative impulse through the condenser C_2' to the grid of valve II. When the grid voltage of valve II decreases its plate voltage increases, a positive impulse through condenser C_2 helps the trigger impulse in making the grid of valve I positive, and the counter is brought over into condition (2). The next impulse will in a corresponding way bring it back to condition (1) again.

A milliammeter in one of the plate circuits shows whether the counter is in condition (1) or (2). From one of the plates impulses can be taken to another scale-of-two counter or, as in the figure, to a thyratron with a counting meter. The counter seems to be very stable and reliable. Any of the elements in the circuit can be changed by at least 20 per cent without harm. For example, the permissible latitude of the grid bias was -14 to -28 v.

The circuit can be triggered by negative impulses also, but only if their amplitude is very large. In the cosmic-ray counter the last valve of the amplifier gave negative impulses, and their sign was accordingly reversed by means of a transformer.

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THE PREVENTION OF THE TRANSMISSION OF SOUND ALONG WATER PIPES

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Received 17 November 1937. Read 11 February 1938

ABSTRACT. Measurements have been made, in the frequency range 50 to 10,000 c./sec., of the transmission of vibration through various lengths and types of rubber hose with a view to determining the value of rubber inserts when used in water systems for reducing the transmission of vibration. The results showed that (1) the insulation obtainable increases with the frequency of the vibration and the length of the rubber pipe; (2) canvas-reinforced rubber is less effective than plain rubber; (3) over the range of diameters tested, the insulation does not vary with the cross-section; and (4) under the conditions of the measurements, sound-transmission through the water contained in the pipe is unimportant.

THE subject of the prevention of sound-transmission along water pipes is assuming greater significance as more and more people decide to reside in hotels or blocks of flats. Noise made in the boiler house, for example, by stoking or, what is probably more important, the pump for circulating hot water, can be transmitted through the hot-water pipes to the radiators and cause a nuisance in rooms remote from the original source of disturbance. Another source of disturbance is the hiss generated by water taps. The water pressure in blocks of flats is frequently quite high, a condition which renders the problem of the hissing of taps and ball cocks very prominent. Sounds of this type are often conducted along the pipes to distant rooms.

The object of this paper is to discuss one method of reducing the transmission of sound by water pipes and to give the results of some experiments made on this subject at the National Physical Laboratory. The method referred to is that of inserting a short length of flexible tubing in the water system, preferably close to the source of noise. This method has been used at the National Physical Laboratory for preventing disturbance in the Acoustics Laboratory arising from the pump circulating hot water. Measurements on this installation⁽ⁿ⁾ have shown that an insulation of some 10 db. against the low frequencies generated by the pump can be obtained by using a flexible insert consisting of a 3-ft. length of rubber hose reinforced with canvas.

The explanation of the insulating action of such rubber inserts is complicated, because transmission along both the pipe and the water column has to be con-

sidered. The insulation against transmission along the walls of the pipe can be calculated⁽²⁾ by using a well-known formula:

$$\text{Insulation } R = \frac{\text{energy of initial vibration}}{\text{energy of vibration transmitted by insert}} \\ = 1 + \left(\frac{r^2 - 1}{r^2 + 1} \right)^2 \sin^2 kl \quad \dots\dots(1),$$

where r is the ratio of the specific acoustic resistances of the metal and rubber pipes, including an allowance for their relative cross-sectional areas; $k = \omega/c$, where ω is the pulsatance of the sound and c the velocity of sound in rubber; and l is the length of the rubber insert.

As regards the insulation provided by the water column, this may be calculated by a formula given by P. J. Korteweg⁽³⁾ for the velocity of sound in a fluid contained in a pipe with yielding walls. The formula is:

$$\frac{c^2}{c^2_R} = 1 + \frac{2ER}{aE_1(1 - 5a/6R)} \quad \dots\dots(2),$$

where c is the velocity of sound in the free fluid, c_R the velocity of sound in the fluid in the pipe, E the elasticity of the fluid, E_1 the elasticity of the walls of the pipe, R the radius of the tube and a the thickness of the wall of the pipe. By combining this formula with formula (1) the attenuation in the water column can be calculated, and under ordinary conditions it is not likely to be more than a few decibels. Before the sound conducted through the water column can be heard, however, it has to be transmitted from the water to the wall of the pipe and at this stage a further attenuation takes place, the magnitude of which cannot easily be assessed. The existence of this additional attenuation, the difficulty of deciding the relative importance of the pipe and water paths, and doubts regarding the elastic constants of rubber hose, indicated the need for an experimental investigation.

In the measurements described below an attempt was made to determine the insulation obtainable from various lengths of rubber insert. Two types of rubber were used and pipes of several diameters were employed. An attempt was also made to determine the importance of the water path by measuring the insulation with and without the presence of a water column.

The experimental arrangement is shown in figure 1. Two 3-ft. lengths of iron pipe joined by the rubber hose under test were supported horizontally on elastic suspensions as shown, the design being such that the area of contact of the support with the pipe and the stiffness of the elastic insulation of the supports were both as small as possible. This arrangement was adopted in order to minimize the damping of the pipe vibrations. One of the lengths of pipe was driven at the end remote from the rubber hose at a series of warbling frequencies between 50 and 10,000 c./sec. The vibration of both pipes was measured at a series of points along them by an electromagnetic vibration detector⁽⁴⁾. The mean square vibration, which is proportional to the energy of vibration, was calculated for each pipe from the results obtained, and the ratio of the two means was taken as the insulation due to the rubber. Check measurements were made upon a 6-ft. length of pipe uninterrupted

by a rubber insert, to confirm that there was no attenuation along the metal pipe itself.

It must be acknowledged at once that this method of determining the insulation due to the rubber insert can be criticized on the ground that such inserts are usually used in connexion with much greater lengths of metal pipe. This is not, as a matter of fact, always the case; for example, a rubber insert is sometimes used near a tap to prevent the water hiss from being carried back along the pipes. As, however, the use of a considerable length of pipe would have introduced experimental difficulties and would have rendered standardization of conditions troublesome, the method of measurement here described was adopted. It is probable that even if the absolute magnitudes should need modification in the light of future investigation, the relative magnitudes will be found reasonably correct.

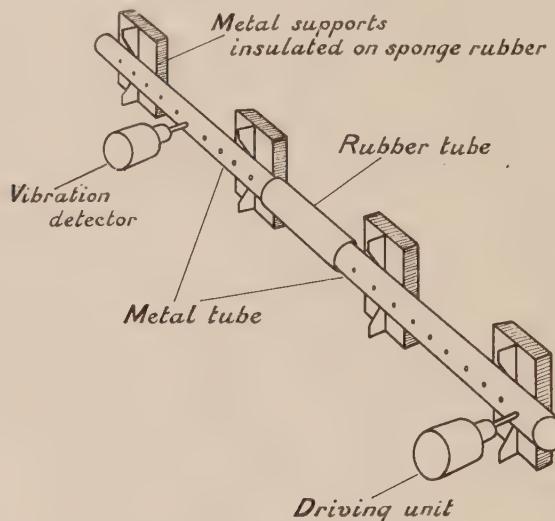


Figure 1. Disposition of apparatus used for measuring the insulation provided by rubber tube inserts.

The results are given in figures 2 to 5, in which the variation of insulation with the length of the rubber is given for a soft red rubber tube and for a black rubber hose reinforced with canvas, respectively. It will be noticed that the insulation is expressed in decibels.* The curves in figures 2 and 3 were obtained by averaging results obtained for two red rubber tubes having walls $\frac{1}{8}$ in. thick and internal diameters of $\frac{3}{4}$ in. and 1 in. respectively. The results obtained with these two tubes were not distinguishable within the limits of experimental error, and the course of averaging them was accordingly adopted. Similarly, the results in figures 4 and 5 were obtained by averaging results obtained with two canvas-reinforced hoses having walls $\frac{3}{16}$ in. thick and internal diameters of 1 in. and $1\frac{1}{2}$ in. respectively. The following general conclusions emerge from the measurements.

* The insulation expressed in decibels is ten times the common logarithm of the ratio of the mean square vibrations in the two pipes.

(1) For a given rubber pipe, the insulation increases with the test frequency up to several thousands of cycles per second and thereafter appears to decrease again. No

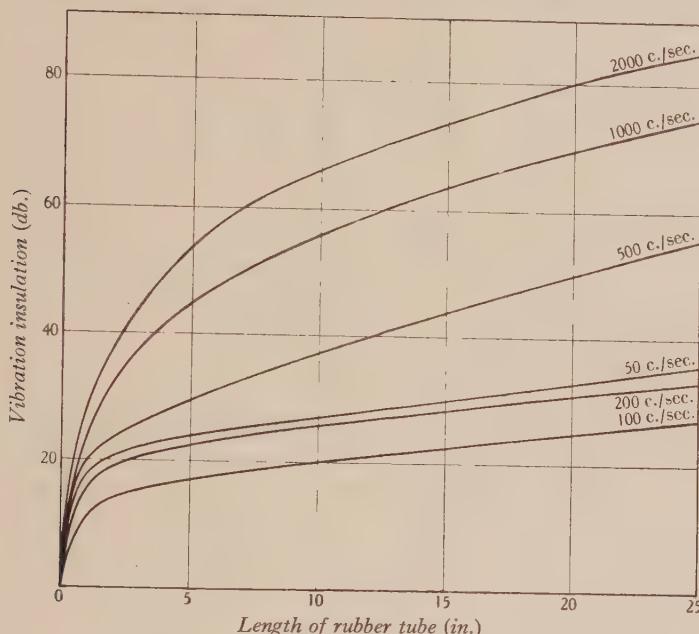


Figure 2. Insulation provided by soft red rubber hose. (Results averaged for tubes having internal diameters of $\frac{3}{4}$ in. and 1 in. respectively.)

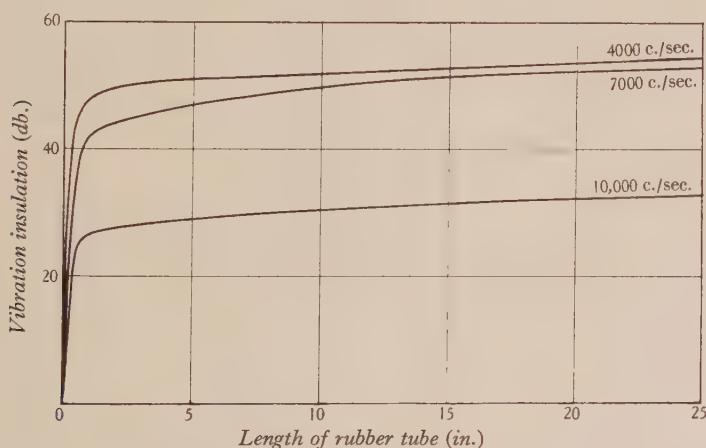


Figure 3. Insulation provided by soft red rubber hose. (Results averaged for tubes having internal diameters of $\frac{3}{4}$ in. and 1 in. respectively.)

satisfactory explanation of this effect was obtained. Tests confirmed that it did not originate in the instruments used for the measurement so that it must, it seems, be ascribed either to a modification in the elastic properties of rubber at high frequencies

or to a change in the mode of sound-transmission through the water or rubber. Actually this frequency region is not important in practice.

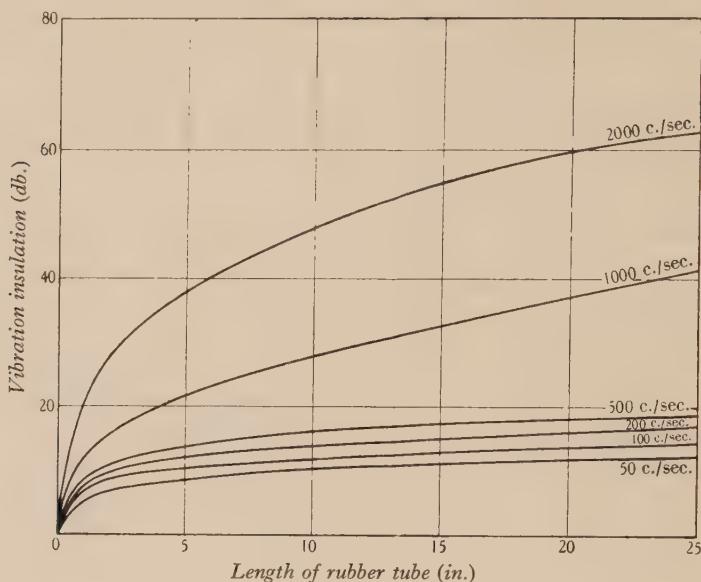


Figure 4. Insulation provided by canvas-reinforced rubber hose. (Results averaged for tubes having internal diameters of 1 in. and 1½ in. respectively.)

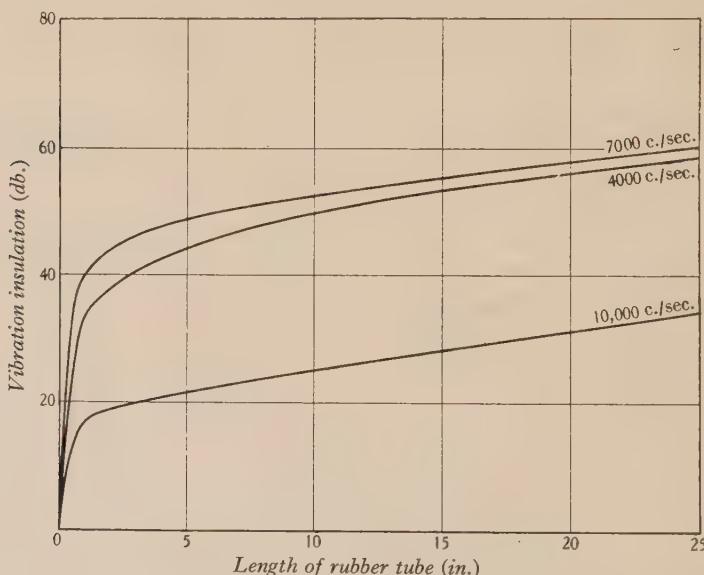


Figure 5. Insulation provided by canvas-reinforced rubber hose. (Results averaged for tubes having internal diameters of 1 in. and 1½ in. respectively.)

(2) At the same test frequency the insulation, on the average, increases as the length of the rubber pipe is increased. There are occasional indications of the

insulation passing through a minimum for certain lengths, but the minima are not well established and could be ascribed as well to resonance effects in the metal pipe as to such effects in the rubber.

(3) Canvas-reinforced rubber, which is stiffer and probably has more internal friction than plain rubber, is not so effective an insulator as the latter. It can, nevertheless, provide quite a reasonable insulation.

(4) Over the range of pipe-diameters tested, insulation does not vary with the cross-section.

(5) Under the conditions of the experiment, conduction through the water column is unimportant, the results being, within the experimental error, independent of whether the pipes contained water nor not.

It will be noticed incidentally that the insulation of 10 db., quoted earlier, obtained from measurements of the attenuation of low-frequency hum by a 3-ft. length of canvas-reinforced hose inserted in a hot-water system agrees with the value which the curves would predict for this length. This result suggests that the curves would be fairly generally applicable to rubber inserts in actual water systems.

The practical significance of these results is that for the greatest insulation a soft rubber is necessary; that for insulation against low-frequency sound a considerable length (of the order of feet) of rubber pipe should be used; and that high frequencies, such as tap hiss, can be dealt with by comparatively short lengths of rubber.

ACKNOWLEDGEMENTS

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DISCUSSION

Dr O. KANTOROWICZ. The author attributes the high insulation value of a rubber hose inserted in a pipe line mainly to the reflection of waves at the boundaries between steel and rubber and between water in the steel tube and water in the rubber hose. Rubber has a high mechanical hysteresis and I think this might play a part, as the energy used by the wave in bulging up the rubber hose, as it travels along the water, will not be delivered back fully. The form of the curves in figures 2 to 5 suggests a mixed mechanism of attenuation. The first steep rise might be due

to reflections as suggested by the author, but the further rise of the insulation must be due to the material in between the reflecting boundaries, and I suggest that it may arise from internal damping in the rubber. It might be possible to reach a decision on this point by using two or more rubber inserts of short length in series, and comparing the {insulation length} curves thus obtained with those published. I do not feel satisfied, however, that the experimental arrangement shown in figure 1 allows of the observation of waves travelling longitudinally, for the transmitter is so set as to put only transverse vibrations into the system, and the receiver is set to pick up only transverse vibrations from the system. I suggest that in this arrangement the pipes with the water as a whole are vibrating transversely, somewhat like strings. This would explain why there is no real difference between full and empty pipes. Filling would merely increase the inertia, thereby lowering both the amplitude for equal energy and the wave-speed along the tube. Neither of these seems to have been measured. At the boundary between rubber and steel, the rubber receiving the same travelling impulse as the steel must move through much bigger amplitudes, as its stiffness and its inertia are so much lower; hence for equal lengths of piping there should be more energy at any time in the rubber than in the steel, and therefore the comparatively high damping capacity of rubber should make itself felt in an accentuated manner.

Dr E. G. RICHARDSON. I am surprised that there is no evidence given by the records of a resonance in the pipe system within the range of frequencies covered. Can the author give us any indication of the natural frequencies of the system sketched in figure 2? It might be possible to work these out on impedance principles, although I suppose that, even if considerably idealized, the system would involve an awkward acoustic circuit of impedances in series and parallel.

Dr R. T. BEATTY. It would be interesting to find out whether the energy was transferred appreciably to the water, or whether the experiment, in effect, dealt with transmission in pipes.

AUTHOR'S REPLY. In reply to Dr Kantorowicz: I doubt whether hysteresis in the rubber is as important as its low elasticity. My reasons are that (1) the attenuations were too high (up to more than 100,000,000, i.e. 80 db.) to be accounted for by hysteresis; (2) canvas-reinforced rubber hose, which presumably has greater hysteresis losses than soft rubber hose, is considerably less insulating, as is shown in the paper. I agree that probably the vibration imparted to the pipe consisted of transverse more than of longitudinal waves, though I think there is no doubt that it is extremely difficult to get one type of vibration without the other. However, in the practical problem of reducing noise from water pipes, transverse waves have the greater importance since they radiate more sound into the air. This was the reason for using the experimental arrangement described.

In reply to Dr Richardson: The resonance of the steel pipes was of the order of thousands of cycles per second. This probably accounts for the apparent loss in insulation of the rubber pipe at frequencies above 4000 c./sec. Calculation of the

resonances of the rubber pipe is difficult owing to uncertainties as to the elastic properties of rubber.

Dr Beatty raises an important point. Possibly one could meet his criticism by driving the water directly by means of a plunger system, and probably an opportunity will present itself for making measurements on these lines. For the present I can only rely upon other measurements (*Engineering*, Nov. 26, 1937) of the insulation provided by a rubber pipe against vibration communicated by a circulating-pump to water in a heating system. The results obtained agreed with the results presented in this paper for a frequency of 100 c./sec. (the frequency of the vibration generated by the pump). There are, of course, theoretical reasons for expecting that conduction of vibration through the water column would be unimportant, namely (1) the fact that such vibration is attenuated by the rubber connexion, (2) the inefficiency of transmission of vibrational energy from water to steel (such transmission has to take place before the sound can be heard), (3) the vibration in the water column must be longitudinal and will on this account be ineffective in generating radial vibration in the steel pipes.

THE TRANSMISSION OF SOUND IN A BUILDING BY INDIRECT PATHS

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ABSTRACT. A description is given of experiments made in a reinforced-concrete building to determine the extent to which sound was transmitted from room to room otherwise than directly through an intervening partition or floor. It is found that operating a loudspeaker in one room generated a sound-intensity in a room 55 ft. away which is not very much less than that in the room next to that containing the loudspeaker. The results show that, in the building considered, indirect transmission between two rooms was comparable with the direct transmission when the intervening partition (in this case a floor) had an insulation of about 50 db. For partitions having a smaller insulation the indirect paths were of less importance.

§ I. INTRODUCTION

CONSIDERABLE investigatory work has now been carried out regarding the construction of sound-insulating partitions and a number of the principles which should be followed are now clear^(1, 2, 3, 4, 5, 6). It is obvious, however, that the intervening partition is not the only path by which sound can travel between two rooms. The flanking walls and floors, for example, must also play their part and there must come a stage at which improvements in the sound-insulating value of the partition alone produces very little effect upon the insulation between the rooms.

For the purposes of this paper, paths by which sound travels between two rooms are divided into the direct path through the intervening partition, and indirect paths through the building fabric.

With the object of obtaining an idea as to the importance of the indirect paths, measurements have recently been made in a block of one-room flats and the results are given below. The building concerned was a ten-storey reinforced-concrete building, the outer walls being solid and having an estimated weight of 70 lb./ft.². Internal partitions were double, consisting of two leaves of light 2-in. building blocks with a 2-in. air space between them.

For the purpose of the measurements a loudspeaker generating a warble note was placed in one room and the sound-intensities in that and a number of other rooms in the building were measured. Measurements were also made of the wall vibration in the majority of these rooms. Frequencies of 200, 700 and 2000 c./sec. were used for the measurements. It was found, however, that the background noise was too high for satisfactory measurements to be made in all the rooms at the

upper two frequencies, owing, presumably, to the greater insulating value of partitions at higher frequencies. The results given below are accordingly, except where otherwise stated, for 200 c./sec. only, these measurements being the most accurate. It may be stated, however, that wherever measurements were possible at the higher frequencies, the general conclusions agreed with those obtained from the measurements at 200 c./sec.

§ 2. TRANSMISSION OF SOUND HORIZONTALLY

In the first series of measurements, the sound transmitted in a horizontal direction was determined, the arrangement of the rooms concerned being as shown schematically in figure 1. The results obtained are given in table 1, in which the air-borne sound intensities in the rooms (measured in decibels above an arbitrary

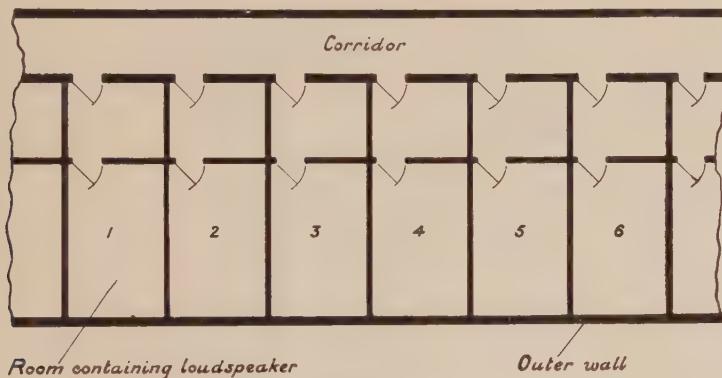


Figure 1.

zero) and the mean vibration of the flanking wall are given. It will be noticed from figure 1 that there was only one continuous flanking wall, and it was the vibration of this that was measured. It was not possible to measure the vibration of the floors or ceilings, but probably, since the building is a monolithic structure, the vibration of the outer wall is representative of that of the floors and ceilings.

Table 1. Transmission of sound horizontally

Room	Approximate distance from centre of room 1 (feet)	Air-borne sound intensity in room (db. above an arbitrary zero)	Mean vibration of flanking wall (db. above an arbitrary zero)
1	—	71	—
2	11	32	53
3	22	24	38
4	33	18	35
5	44	20	34
6	55	18	30

It will be noticed that after room 2 there is only a small drop in sound-intensity as the distance from room 1 increases. This is clearly due to sound-transmission by

indirect paths. Confirmation of this view is given by the fact that, within the limits of experimental error, the air-borne sound intensity is approximately proportional to the vibration of the flanking wall.* It will be noticed incidentally that the rate of attenuation of structure-borne sound in the flanking wall is about $\frac{1}{2}$ db./ft. for the frequency (200 c./sec.) used for the measurement.†

§ 3. TRANSMISSION OF SOUND VERTICALLY

A second series of measurements was made in the same building upon the transmission of sound in a vertical direction. The arrangement of the rooms concerned is shown schematically in figure 2. The loudspeaker was operated in room 1

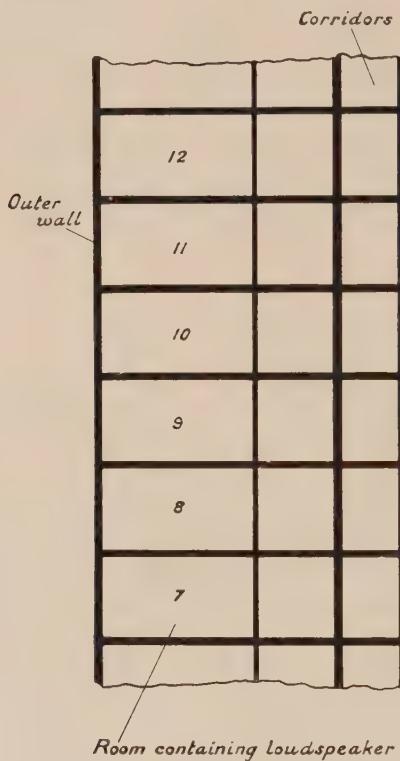


Figure 2.

and measurements of the intensities of the air-borne sound and the wall vibration were made as before. The results obtained are given in table 2. It will be noticed that the decrease of the intensity of air-borne sound with increasing distance is very much the same as for horizontal transmission, considerable sound reaching rooms

* The results are given in decibels and, in consequence, this proportionality is exhibited by the difference between the respective readings being approximately constant.

† A. Gastell⁽⁷⁾ gives a value of 2·5 phon per metre for the attenuation of impact sounds in concrete.

remote from the room containing the loudspeaker. The rate of decay of structure-borne sound in the walls is about $\frac{1}{2}$ db./ft., as for horizontal transmission.

Table 2. Transmission of sound vertically

Room	Approximate distance from centre of room 7 (feet)	Air-borne sound intensity in room (db. above an arbitrary zero)	Mean vibration of flanking wall (db. above an arbitrary zero)
7	—	75	—
8	9	29	44
9	18	27	45
10	27	21	34
11	36	24	33
12	45	18	28

4. COMPARISON OF HORIZONTAL WITH VERTICAL TRANSMISSION

On comparison of tables 1 and 2 it is noticeable that whereas for vertical transmission, table 2, the sound-intensities in rooms 8 and 9, next and next-but-one to the room containing the loudspeaker, are very similar, when horizontal transmission is considered, table 1, there is a considerable difference between the intensities of the sound in the corresponding rooms, rooms 2 and 3. This suggests that, as regards sound-transmission between two rooms in a vertical direction, the indirect paths are

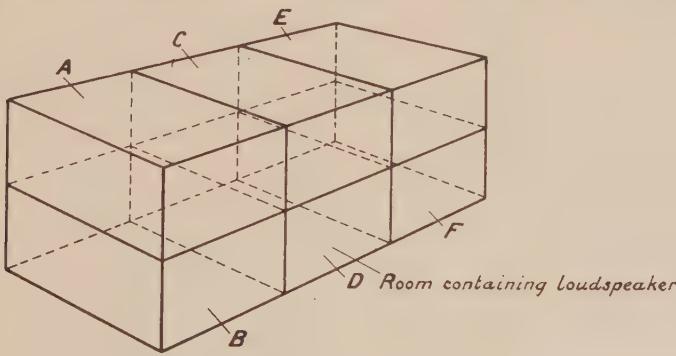


Figure 3.

comparable with the direct path through the intervening floor. On the other hand, in the case of horizontal sound-transmission, the direct path through the partitions is definitely more important than the indirect path. In fact, an improvement in the sound-insulating properties of the partitions could usefully be made, but an improvement in the insulation provided by the floor against air-borne sound would have little value.

To obtain another value for the sound transmitted by indirect paths, measurements were made in a group of six rooms situated as shown in figure 3. With the loudspeaker situated in room D, measurements were made of the intensities of air-borne sound in rooms A, B, C, E and F. As is shown in the diagram, sound will

reach rooms *A* and *E* by indirect paths only. The indirect paths are in this case somewhat different from the indirect paths which exist during horizontal transmission, in that there is only one common floor in the case of diagonal transmission. The other common floor is, however, replaced by the common vertical partition. The contributions by these paths are probably about the same as they would be if the rooms had been adjacent and on the same level. The results obtained are given in table 3, in which is shown the mean sound-insulation against sound transmitted in horizontal, vertical and diagonal directions.

Table 3. Comparison of horizontal, vertical and diagonal transmission for a set of six rooms

Frequency (c./sec.)	Mean insulation against sound transmission (db.)		
	Horizontally	Vertically	Diagonally
200	41	44	49
700	41	49	49
2000	56	56	> 56

§5. GENERAL CONCLUSIONS

When these results are averaged it appears that, in the reinforced-concrete building studied, the sound transmitted by indirect paths was not of great importance as far as horizontal transmission was concerned, but was appreciable for vertical transmission, the difference arising from the fact that the floors were on the average 6 db. better sound insulators than the partitions. In other words, there would be an advantage in increasing the insulation of the partitions from their present mean value of 44 db. up to about 50 db., but no increase beyond this point would be of any value unless some attention was paid to indirect paths of sound transmission.

As regards the possibility of predicting the magnitude of the indirect transmission, it is early yet to attempt any generalization. It is significant that the mean insulation against indirect transmission was about 50 db. in the building studied, a figure which is the same as the insulation that would be expected from the flanking walls and floors (each weighing 50 to 70 lb./ft²) if used as partitions between two rooms. That is to say that it seems, at least in the case of monolithic concrete structures, that the vibration acquired by a wall or floor when air-borne sound falls upon it can be transmitted with little attenuation, along the length of the wall, to neighbouring rooms.

§6. ACKNOWLEDGEMENTS

The author wishes to express his thanks to Dr G. W. C. Kaye, Superintendent of the Physics Department, for his encouragement and to Dr A. H. Davis for criticism and advice. Mr R. Berry rendered valuable assistance in setting up the apparatus and making the measurements.

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DISCUSSION

Dr R. SAMUEL. Would it be possible to remeasure the same building after a year or two, in view of the fact that concrete changes its inner (chemical or crystal) structure after that time?

AUTHOR'S REPLY: There is evidence that the sound-transmitting properties of building structures change in the first few weeks. There would be some interest in measuring them again after a year or so, but unfortunately this is rarely possible since measurements such as those described in the paper can only be made when the buildings are unoccupied.

THE ELECTRICAL REPRODUCTION OF IMAGES BY THE PHOTOCONDUCTIVE EFFECT

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ABSTRACT. It was recognized in the early days of television that a modified form of cathode-ray oscilloscope might be used as a transmitting device, the electron beam serving as a means for exploring rapidly the image to be transmitted. A. A. Campbell-Swinton⁽¹⁾ was amongst those who foresaw this future use of the cathode-ray tube and he attempted, though unsuccessfully, to produce a transmitting tube by replacing the fluorescent screen by a layer of light-sensitive selenium⁽²⁾. Several variations have been suggested in patents⁽³⁾ but no successful television transmitter using the photoconductive effect has appeared. The present paper describes some investigations into this method of producing picture signals, in which a number of light-sensitive materials were examined.* During its preparation two accounts have appeared in which the same method of signal-production has been investigated and results of a similar nature have been observed^(4, 5).

§ 1. PHOTOCOnductivity

ALARGE number of inorganic solids have been found to possess photoconductive properties similar to those first observed in layers of suitably annealed selenium. The processes involved are very complicated, but the work of Gudden and Pohl⁽⁷⁾, who investigated the effect in single crystals has contributed to a clearer understanding of the effect. They classified two types of crystal, those (idiochromatic crystals) which give a photoelectric conductivity immediately on illumination in the normal state, and those (allochromatic crystals) which only do so as a result of the introduction of foreign atoms or particles into the crystal lattice by certain external agencies. The former are crystals of high refractive index, and include sulphides and oxides of many heavy metals and some crystalline modifications of some pure elements⁽⁷⁾. This paper is concerned with the investigation of materials entirely of this class.

The current observed to flow under illumination was separated by Gudden and Pohl into two components, the primary photoelectric current, and the secondary current. The primary current corresponds to the actual internal photoelectric phenomenon and can be separated in certain crystals into (*a*) the negative primary current, which is the liberation of the electrons by the light and the motion of

* A demonstration of the use of the photoconductive effect in a television transmitting tube, based on the work here described, was shown at the Television Exhibition at the Science Museum in South Kensington from June to September, 1937.

these electrons through the crystal lattice, and (b) the positive primary current which is the supplementation of these electrons in order to neutralize the space charge formed by such excitation.

The passage of the primary current may produce a change in the lattice and cause a decrease in resistance, thus giving rise to a secondary current. This differs in several respects from the primary current. It does not, for instance, follow the changes of light-intensity without delay. It does not vary linearly with the light-intensity, and it may be several times bigger than the primary current, which approaches a value equivalent to the number of absorbed light quanta. Secondary currents predominate in cases where there are many centres of disturbance in the lattice, so that since most of the work to be described was done with polycrystalline powders, it appears probable that secondary currents are the effective ones.

§ 2. EXPERIMENTAL METHOD

The materials for testing were deposited as a layer on a conducting metallic base, the signal plate M , figure 1, and mounted in an envelope E which could be evacuated. In some cases a transparent metal layer was used as the signal plate to allow illumination of the test layer from either side. Also mounted in the envelope was a simple type of electron gun G which produced a cathode-ray beam to scan the test surface with a pattern of about 200 lines 50 times per sec. The accelerating

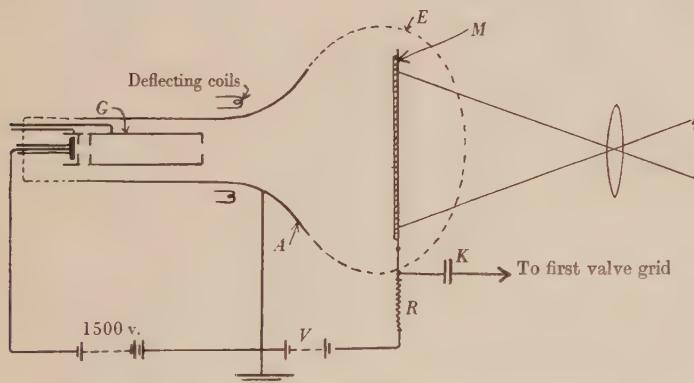


Figure 1. Experimental arrangement of test apparatus.

potential used was 1500 v. The secondary electrons emitted from the layer were collected on an anode A on the walls of the envelope. The signal plate was connected to earth by a resistance R of about 1 megohm and a battery V which supplied the potential necessary for the collecting of the secondary electrons. The current passing through the layer caused a potential-drop across the resistance, the signal plate end of which was connected through a condenser K to an amplifier. The output of this amplifier was used to modulate the beam in a normal cathode-ray receiver tube scanned synchronously with the tube containing the materials under test. As the scanning beam passed from illuminated elements to unilluminated ones

the changed resistance caused the current down the signal-generating resistance R to be modulated, and a picture signal appeared on the receiving tube.

Many materials were tested in a vacuum tube pumped continuously, the plate M in this case being sealed on to the end of the envelope with Apiezon sealing compound Q , and being easily removable. In other cases the materials were tested in sealed-off tubes after a rigorous baking treatment.

The materials in general were prepared for testing by a chemical precipitation process followed by heating in nitrogen to about 900°C . A long grinding in a ball mill followed, after which the layer was produced from the fine aqueous suspension either by spraying or settling on to the metal plate. Some materials required special treatment, and for these cases notes on the preparation are given in table 1 which presents the general results.

§ 3. RESULTS OF EXPERIMENTS

By the method described a large number of materials were tested, some being known photoconductors and others those which might be expected to show such an effect. They are listed in table 1, and the form in which each was tested is noted.

In many cases definite signals were observed when a strongly illuminated pattern was projected on to the test layer. It was found that if the anode A was held at a potential in the neighbourhood of M , or even negative to M , in general weak signals were obtained in such a direction that increase of illumination caused negative potential pulses on the signal plate. With an amplifier having an even number of stages, therefore, a bright spot on the layer appeared as a dark spot on the received picture. Such signals will be called negative signals. When the anode was made increasingly positive with respect to M , so that secondary electrons were collected, the signals were found to disappear for a certain voltage between about $+10\text{ v.}$ and $+30\text{ v.}$, the actual value depending on the geometry of the tube. With further increase in V the signals reappeared and were of the opposite sign, i.e. increasing illumination caused positive potential pulses on the signal plate. They increased in magnitude with increasing V up to about $V=50\text{ v.}$, and in some cases passed through a maximum value.

The strong signals were found in most cases not to disappear instantaneously on cutting off the light but to die down gradually in a time amounting to several seconds. This lag was not interpreted as being wholly due to the known lag of the photoconductive effect but was attributed to the comparative slowness of the potential-changes which were produced by scanning, in a manner to be explained later.

The last column of table 1 contains notes on the observed behaviour of the tested materials. Of these, zinc selenide proved to be the most sensitive, and on it most observations were made. More detailed results will be described and the mechanism of the production of signals will be discussed with special reference to this material. The region of the spectrum which produced the observed signals

was found approximately by the direct use of colour filters in the incident light beam, and the results are noted in column 3.

Table I

Material	Preparation for testing	Observations
Selenium	Layer deposited by evaporation in vacuum followed by annealing at 180° C. in air	Very faint signals observed for small + or - values of V . Sensitive to yellow-orange region of the spectrum
Zinc sulphide	Standard fluorescent preparations used	Strong signals observed in ZnS, ZnS-Cu, ZnS-Mn, ZnS-CdS-Cu but not in ZnS unheated.* Sensitive in blue-violet range
Cadmium sulphide	Normal preparation	Signals produced by red-yellow region of spectrum
Thallium sulphide	(1) Precipitated and deposited as sprayed layer without oxidation (2) Layer oxidized by heating in air†	No signals
Antimony sulphide	(1) Precipitated red crystalline form heated in nitrogen at 200° C. (2) Naturally occurring mineral antimonite	Faint signals obtained with little lag and produced by far-red and infra-red light
Zinc selenide	(1) By direct combination of elements (2) By precipitation	Fairly strong signals produced by far-red and infra-red light
Cadmium selenide	Normal preparation heating, in nitrogen to 700° C.	Faint trace of signal obtained
Zinc telluride	Direct combination of elements	Most sensitive material tested. Sensitivity mainly due to yellow region of spectrum
		Faint signals obtained due to red and infra-red light
		Trace of signals obtained

* Zinc sulphide unheated has no fluorescent properties. "ZnS-Cu" etc. refer to zinc sulphide activated by trace of copper etc. to produce fluorescence.

† As in the commercial Thalofide cell.

The following materials were tested but gave negative results. (1) Silver sulphide prepared both by precipitation with subsequent heating to 500° C. in nitrogen, and by the direct action of hydrogen sulphide on silver. (2) Cupric sulphide, cupric selenide, silver selenide, cuprous iodide prepared by normal precipitation followed by heating. (3) Silver chloride prepared on silver electrolytically. (4) Aluminium oxide prepared by anodic oxidation. (5) Cadmium oxide from the heated carbonate and antimony oxide sublimed from the commercial product. (6) Zinc orthosilicate (willemite) and calcium tungstate, i.e. standard fluorescent preparations. (7) Galena, molybdenite, bornite, copper pyrites, i.e. naturally occurring rectifier crystals.

The oxides of copper were tested in various forms and signals were obtained whose general characteristics differed from those obtained with all the other materials tested.

Cuprous oxide. (1) This substance was prepared as a layer on a copper base by roasting in air and afterwards dissolving off the top layer of cupric oxide. No

signals were obtained until the layer had received some special treatment, such as being subjected to heavy bombardment with a cathode-ray beam, or had received a sputtered layer on its surface in a hydrogen discharge. Signals were then obtained which were positive over the whole range of V , fairly strong and quite free from lag. (2) The cuprous oxide crystals removed from such a plate and sprayed after grinding gave no signals. (3) A sprayed layer of crystals precipitated from cupric sulphate gave no signals though weak signals appeared after heavy bombardment with a cathode-ray beam.

Cupric oxide. (1) This was formed on the surface of a cuprous oxide layer by roasting. Weak signals were observed, opposite in sign to those in zinc selenide and free from lag. (2) The same substance was prepared by heating carbonate at 1000°C . This also gave faint signals.

§ 4. ZINC SELENIDE

(a) *Method of preparation.* The method of preparing zinc selenide by direct combination of the elements has the advantage that hydrogen selenide with its unpleasant physiological properties is avoided. It is however unsatisfactory as very little control is possible, and for accurate working it was necessary to adopt the method of precipitation.

The hydrogen selenide was prepared by the action of water on aluminium selenide and passed into a solution of zinc ammonium chloride which had been highly purified to eliminate heavy metals and other impurities. When an excess of hydrogen selenide was present the zinc selenide was filtered off, washed thoroughly, and dried at 110°C . It was then ground to a fine powder and heated in a tube furnace in an atmosphere of nitrogen to 900°C . For test purposes the resulting product was ground in a ball mill in aqueous suspension for 3 hr., and then sprayed or settled in the manner mentioned above.

The effect of the presence of traces of copper and silver was tested by the addition of 0.01 per cent of these metals to the selenide. Little effect on the photoconductive properties was observed.

The effect of temperature of *activation*, as the heating process is called in fluorescence work, was tested over the range 110 to 1100°C . The material heated at 110°C . gave only very faint signals, but good signals differing little in strength were obtained over the range 500 to 900°C . A decrease in efficiency for temperatures over 1000°C . was observed, which may be due to an increase of particle-size in the test layer, since the material was more resistant to grinding.

In order to produce a sufficiently fine material for settling, long grinding was necessary and tests were made of the stability of the photoconductive properties of zinc selenide under this treatment. Samples were ground for periods up to 50 hr. but little decrease in the photoconductivity was observed. Under settling conditions the reactivity of the selenide with the metal base proved troublesome, but the use of gold-plated signal plates prevented such disturbance.

Despite the attempts to obtain reproducible results there was at first a large

amount of unexplained variation. It seems probable that this was due to the instability of the selenium compounds during the precipitation process. Three comparison preparations were made to test this supposition. In the first the precipitation was carried through in an enclosed apparatus from which the air had been expelled with nitrogen and then after the precipitate had been filtered and washed rapidly, it was dried in a vacuum desiccator. The second precipitate was filtered and washed slowly and dried at 110° C. in air. The third precipitate was allowed to stand for 2 days and then treated like the second. The colours of the dried materials were respectively pale yellow, pink, and dark red, owing to the presence of varying quantities of free selenium. All were then heated to 900° C., ground in a ball mill, and tested. The sensitivities of the three samples were in the ratio 1 : 10 : 20. Another test was made, the free selenium being washed out from the last material with sodium cyanide, while the zinc selenide was left as a white precipitate. This after standard treatment gave only very weak signals.

From these results it appears that the presence of free selenium during the activation process plays an important part in the development of the photoconductive properties of zinc selenide. The exact function of the selenium is not clear. No free selenium was detected in the final product by analytical methods, and it is improbable that any was left after the activation process. This view is supported by the observation that zinc selenide gave good signals even after evaporation in a high vacuum had occurred.

(b) *Experimental observations on zinc selenide.* The following observations were made on the signals obtained from zinc selenide. (1) For values of V in the range -200 v. to about +10 v. negative signals were obtained with a maximum value at about $V=0$. Above this was a short range in which no signals appeared, while from about +20 v. to +200 v. strong positive signals were obtained. These were greatest at about +50 v., being then 10 times larger than the best negative ones obtained with small values of V . (2) For a given value of V the signal is proportional to the current in the scanning beam. (3) The signals did not reach their maximum value immediately on the illumination of the test layer, and on the switching off of the light they disappeared only gradually. This lag phenomenon was negligibly small when V was small or negative, but became very pronounced when V became increasingly positive and attained a value of several seconds when V was +50 v. The lag decreased continuously with increase in the scanning-beam currents up to at least 10 μ A. (4) The relation between signal-size and illumination showed a departure from linearity as the illumination increased and a saturation effect for values of the illumination of about 70 ft.-candles on the test layer. (5) The optimum thickness of the test layer was found to be approximately 2 to 3 μ . For greater thickness the light penetrates only a portion of the layer, the rest retaining its high dark resistance. The reduction in sensitivity for smaller thicknesses was due apparently to the fact that owing to the finite particle-size, thinner settled layers were not completely covered. The absorption of light in a wedge-shaped evaporated layer was observed. It appeared that the most sensitive region of the spectrum lay on the long-wave end of the absorption band (a usual property of

idiochromatic crystals) and that the depth of penetration was about 2μ . Layers of the selenide evaporated in high vacuum from a tungsten spiral were found to give strong signals if the thickness was of this order. The signals disappeared for large values of V and had a longer lag than had those observed in the settled layer. It may be noted that for layers of this thickness the distance between the centres of adjacent picture elements during scanning with 200 lines of width 0·3 mm. is large compared to the distance through the layer. On this basis the resistance of the single element is in later sections deduced after the resistance along the layer has been neglected. In practice the pictures obtained were very sharp, the conductivity along the surface being negligibly small.

§ 5. MECHANISM OF SIGNAL-PRODUCTION OF ZINC SELENIDE

A consideration of the behaviour of a highly resistive layer under bombardment by a cathode-ray beam together with a recognition of its photoconductive property gives a satisfactory explanation of the above observations.

As the cathode-ray beam passes over the layer its front surface takes up a potential at which there is equilibrium between the number of electrons arriving in the beam, the number lost to the collecting electrodes as secondaries, and the number passing through the layer to the signal plate. If the resistance through the layer is high, the potential of the front surface is practically that which causes the surface to lose to the collecting anode one secondary electron per primary arriving. The secondary emission from the selenide due to electrons having an energy of 1500 v. has been measured by a ballistic method, and the ratio of secondary to primary electrons is about 2 : 1. An insulated surface of such a low secondary emission would, if bombarded, take up an equilibrium potential several volts negative with respect to the collecting electrode. This potential is the value of V for which no current flows through the signal plate lead, and was found, in the geometrical arrangements used, to be between 10 and 20 v. This was also the value of V for which no signals were obtained.

For other values of V a potential-difference will exist across the layer, and in the intervals between successive passages of the electron beam the potential on the front of the layer will approach that of the signal plate. The rate of leakage will depend on the resistance and capacity of the layer.

The specific resistance of the selenide was estimated by the following method. If potential differences exist over the surface of the layer when it is scanned by the beam, picture signals are obtained, since the loss of secondary electrons to the anode is not constant and varying charges are induced on the signal plate through the elementary capacity. The layer was, therefore, scanned in the dark with a potential-difference V of +50 v. between anode and signal plate. The front of the layer was then charged up uniformly until a potential-difference of perhaps 40 v. existed between the front and the back of the layer. The scanning beam was then cut off and a brightly illuminated pattern was projected for a short time on to the layer. The illuminated parts leaked away rapidly to the signal-plate potential,

the dark parts only slowly. After such illumination a picture could be seen on scanning again if the layer remained in the dark without further illumination up to a period of about 8 min. This period indicates the time taken by the charge on the dark elements in leaking away to the signal plate. We have assumed that this time represents about three times the time-constant of the leaky-condenser system of which the element is ideally composed, and if a value of about 6 is assumed as a reasonable one for the dielectric constant of the selenide, an estimate of $10^{14} \Omega\text{-cm}$. is obtained for the specific resistance in the dark.

The memory time decreased considerably if there was a steady illumination of the test layer after the flashing-on of the picture, and was reduced to about 0.01 of its dark value under an illumination of about 80 ft.-candles. This corresponds to a specific resistance of about $10^{12} \Omega\text{-cm}$. under such illumination. Attempts to measure the specific resistance directly were not very successful owing to the

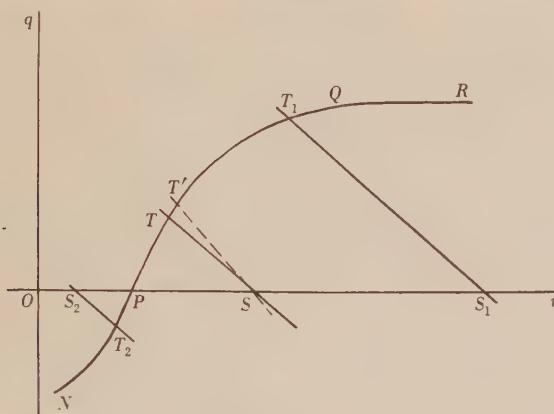


Figure 2.

difficulty of making a satisfactory contact with the layer, but the evidence obtained tended to confirm the conclusion that the specific resistance was of this order.

Under the conditions of the experiment, therefore, during scanning with 200 lines, the element will be about 0.01 mm. square and about 0.002 mm. thick, and the element resistance through the layer will be of the order $10^{13} \Omega$. in the dark and possibly of the order $10^{11} \Omega$. in the conditions of maximum illumination. Under equilibrium conditions the potential of both the dark and light elements will reach such a value that the charge gained during the passage of the scanning beam equals that lost during the interval between successive scans. These will be different for the light and dark elements, and the difference gives rise to the picture signal.

The way in which these signals vary as the potential on the anode is varied can be simply deduced from the curve shown in figure 2. The curve $NPQR$ represents the relation between q , the net charge which each element receives as the scanning beam passes once over it, and v , the voltage-difference between the front of the selenide layer and the collecting anode. The general shape of the curve can be

deduced simply from observations on the collection of secondary electrons under steady bombardment and under various applied collecting potentials.

The loss in charge from the element initially at voltage v below the collector, due to leakage between successive scans, will be given by an expression of the form

$$\begin{aligned} q' &= Q_0 - Q = Q_0 - Q_0 e^{-t/CR} \\ &= C(V-v)(1-e^{-t/CR}) \\ &= \frac{t}{R}(V-v) \text{ approximately.} \end{aligned}$$

Here t is the time between two successive scans, Q_0 is the initial charge on the element given by $C(V-v)$, since $(V-v)$ is the initial potential-drop across the layer. CR is the time constant of the decay of charge on the leaky condenser by which each element is represented. Thus

$$q' = k(V-v) \quad \dots\dots(1),$$

where, for a given element, k is a constant inversely proportional to the resistance of the element. To find the value of q for the equilibrium case, in which the charge gained per impact of the beam equals that lost between scans, equation (1) is plotted as the line ST in figure 2, the ordinate of the point of intersection T giving the charge lost and replaced in each complete frame period. The graph of equation (1) crosses the v -axis where $V=v$, so that for different potentials of the collecting anode relative to the signal plate the point S will have varying positions along Ov . S_1T_1 will represent the line for the case in which, say, $V=60$ v., and S_2T_2 will do so for the case in which $V=5$ v. The slope of the line is inversely proportional to the resistance of the element; that is, it is proportional to the illumination. ST , ST' represent the graph of equation (1) under two conditions of low and high illumination for example.

For an element in the dark the slope of the line ST is so small that the point T is always very close to P , whatever the value of V . The ordinate of the point T for an illuminated element, therefore, will be proportional to the signal obtained from that element.

From figure 2 we can thus deduce the following conclusions which agree with the experimental observations. (1) No signals will be obtained if V has a value at which the number of secondary electrons collected equals the number of primary electrons in the scanning beam (that is, if S and P coincide). (2) For increasingly positive values of V the signal-size will increase to a certain maximum in the positive direction. (3) For values of V below P the signals will become negative, since the surface now loses charge on being scanned. The reason for the fact that strong negative signals are not obtained and for the fact that they do not increase with decreasing V is probably that the electrons spread on to the brightly illuminated parts, which are in this case positive with respect to the dark parts. The signal plate becomes positive with respect to the front of the layer in this region, and catches electrons through cracks and at the edges, and again causes a reduction of signal. (4) Increase of illumination causes the point T to move along towards R .

even if the potential V is held constant. Satisfactory reproduction of half tones in the picture will be obtained, therefore, only if T is on the sloping part of the curve. There is a flattening off in the signal illumination curve for illuminations above about 60 ft.-candles if $V = 50$ v., and at lower illuminations if V is greater than this.

The incidence of lag also is explained by this mechanism. When the light is first switched on, the signal obtained will grow in intensity until the potential on the front of the layer has been reduced from its dark value to its value for a light element. The time for this will be small if V has a value near to the potential for zero signal, but big if V is big, when $V = 50$ v. it can be expected to be an appreciable fraction of a second.

After the light is switched off, even if the resistance instantly returns to its dark value, a signal will be obtained until the beam has charged up the element so that there is no appreciable difference between its potential and that of an element previously unilluminated.

This also increases with increasing values of V , being negligible for small values. If V is about 50 v. the change of potential produced by the impact of a scanning beam of $1\mu\text{A}$. under steady conditions on an illuminated element is only of the order of 0.1 v., but in order to charge up the layer to its dark steady condition a potential-change of possibly 10 v. is necessary, and the signal will, therefore, be observed for 50 or 100 scans after the light has been turned off. In order that the tube may be effective for television transmission it would be necessary to use a beam current large enough to charge up the layer in only one or two scans. Such currents are enormous compared to those normally used in such devices.

§ 6. BEHAVIOUR OF OTHER MATERIALS

According to the mechanism sketched above it appears that if signals are to be obtained for the region in which V is large, a certain minimum dark specific resistance of the layer is necessary. If the element-resistance is too small, both dark and light elements will leak sufficiently during a frame-time to cause saturation of the secondary electrons to the collecting anode on the next impact of the scanning beam. No signals due to illumination will then be obtained. If the dark specific resistance of the material is less than about $10^{10}\Omega\text{-cm}$., no signals will be obtained for values of V above about 50 v. This appears to account for the behaviour of some materials in which the signals disappeared for large values of V , the case of evaporated zinc selenide layers being one example. Even if the specific resistance is smaller than this value, however, the potential-differences between illuminated and dark elements will give rise to signals if V is in the region where the secondary electrons are not saturated. These signals will be weak and of short lag, and no memory can be expected. The signals obtained on annealed layers of selenium had these characteristics and were only about $1/20$ as sensitive as those obtained in the selenide.

It appeared necessary in certain cases to suggest an additional mechanism for the production of signals, notably in the case of the cuprous oxide layers formed by the oxidation of solid copper plates. The low specific resistance of the cuprous

oxide will account for the lack of signals in the untreated state of the layer. The effect of treatment in a sputtering-chamber or by heavy bombardment by cathode rays is believed to be due to the formation of a blocking layer of high resistance on the surface⁽⁸⁾. Under the influence of light, electrons would pass from the cuprous oxide across this blocking layer, causing the front surface to acquire negative charges. Scanning by the electron beam would then restore the elements to some common equilibrium potential more positive than the potential of the light elements. Positive potential pulses would be produced in the signal plate, giving the observed positive signals. It is possible that both the photovoltaic and the normal photoconductive effects are concerned in certain cases, but the main observations appear to be capable of adequate explanation on the lines suggested above.

§ 7. ACKNOWLEDGEMENTS

These experiments have been carried out in the Research Laboratories of Electric and Musical Industries Limited, Hayes, and the authors wish to express their indebtedness to Mr I. Shoenberg, Mr G. E. Condliffe and the staff of the Laboratories for their encouragement and assistance in the investigation.

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DISCUSSION

Mr W. H. ALDOUS. Can the authors give any idea of the uniformity to be obtained in the photoconductivity over the surface of a single screen, and whether it compares favourably with the uniformity of emission over a normal photoemissive surface? To what do the authors ascribe the activation of the cuprous oxide under cathode-ray bombardment?

AUTHOR'S REPLY. The background obtained in these transmitting tubes proved to be serious. This background was due not to variations in photoconductivity but to irregularities in the layer, depending on the size of the settled particles, and to chemical action between the selenide and its supporting layer. An evaporated layer of selenide showed a considerable improvement on the settled layer in this respect. The activation of the cuprous-oxide layer under cathode-ray bombardment is presumed to have been due to removal of excess oxygen from the surface layer of the cuprous-oxide crystals.

THE EQUILIBRIUM OF A BALL SUPPORTED BY A VERTICAL AIR-JET

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ABSTRACT. Experiments on the equilibrium of a ball supported by an air-jet are described. The forces acting on the ball are obtained from pressure-distribution curves.

WHEN a light celluloid ball, of the kind used in table-tennis is placed in the stream of air issuing from a vertical jet, the ball is supported at a height of several centimetres above the jet and oscillates slightly both up and down and from side to side about its position of equilibrium. If the jet has been made by drawing down a glass tube it is frequently found that in addition to its oscillatory motion the ball spins rapidly about an approximately horizontal axis. This rotation is not observed when an accurately made brass jet is used and is thus probably due to a lack of symmetry in the glass jets.

The equilibrium of the ball has been studied by measuring the pressure exerted on different parts of the surface of a similar ball held in various positions both on and off the axis of a vertical jet. Three jet-sizes were used, the orifices being cylindrical, 1 cm. in length and of internal diameter 0·18, 0·25 and 0·33 cm. respectively. The jets were threaded to fit on the end of a vertical brass tube which could be moved either vertically or horizontally in a slide and was joined by rubber tubing to a small Cenco compressor. The ball, 3·8 cm. in diameter, was supported above the jet by a horizontal brass tube about 0·2 cm. in external diameter and coaxial with a diameter of the ball to which it was fastened with Durofix. The tube communicated by a small hole with the inside of the ball, which was itself perforated with a small hole lying in the diametral plane normal to the supporting tube. One end of the brass tube was closed and the other was connected by a short length of narrow rubber tubing to the manometers—a simple U-tube and a tilting gauge, both containing xylol. The pressure, above or below atmosphere, measured by the manometers is thus very nearly the same as the pressure exerted by the air stream on the surface of the ball in the region of the hole. By rotating the ball and supporting tube about their common axis the variation of the pressure over the surface could be observed, the position of the hole being read on a circular scale. The supports did not appreciably disturb the flow of air round the ball.

In an experiment with the jet of diameter 0·25 cm. and the compressor running at full speed, a free ball was supported with its centre approximately 13·5 cm. above

the top of the jet. The variation of the pressure over the surface when the ball was in this position is shown in figure 1, in which the circumference of the ball is indicated by the circle and the axis of the jet by the arrow. The excess pressure above atmosphere is measured outwards from the circumference along the radius. Readings of pressure were taken at least every 10° and the experimental points lie extremely close to the smooth curve shown. A positive pressure is experienced by the lower part of the surface of the ball up to the point at which the radius makes

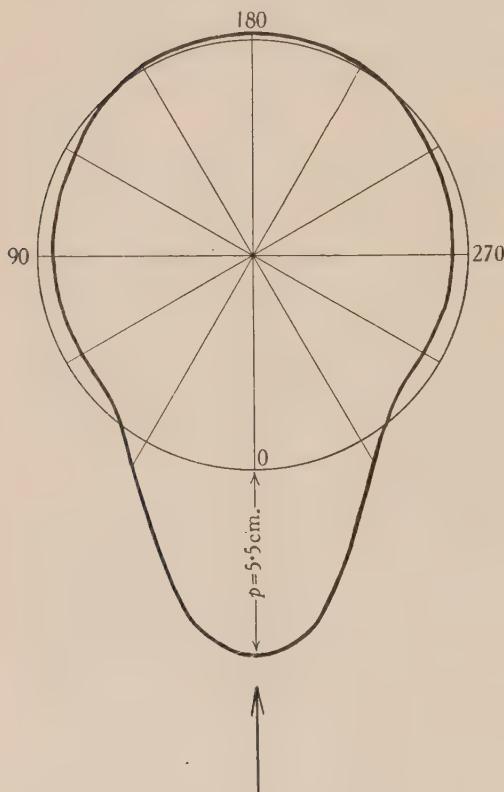


Figure 1. Pressure-distribution with the centre of the ball on the axis and 13.5 cm. above the jet.

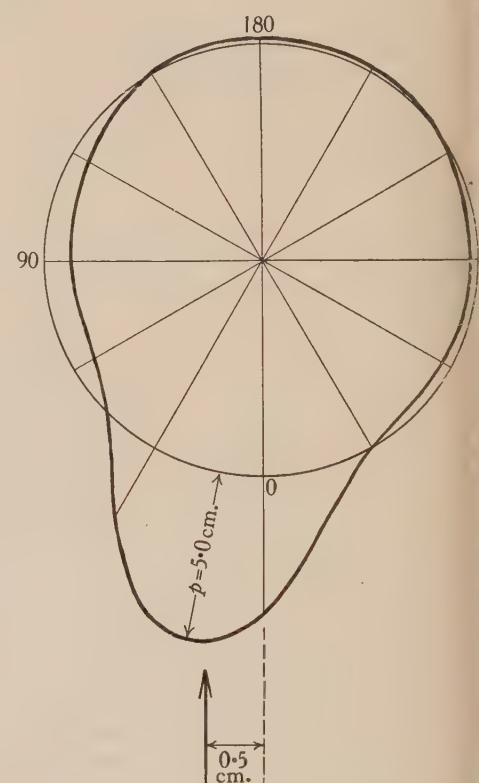


Figure 2. Pressure-distribution with the centre of the ball 0.5 cm. off the axis and 13.5 cm. above the jet.

an angle of approximately 40° with the vertical. From roughly 40 to 140° there is a slight vacuum, while the top of the ball experiences a very small positive pressure of the order of 0.1 cm. of xylol.

The resultant upward force acting on the ball can be determined by graphical integration of the vertical component of the pressure over the whole surface of the sphere. The force obtained in this way is approximately 4.5 g. wt., whereas the weight of the ball is approximately 3.0 g. The agreement is perhaps as good as can be expected. The discrepancy may be largely attributed to the fact that the pressure measurements are probably not accurate to better than 10 per cent in the region from 30 to 180° , whereas this region is extremely important in the calculation

of the resultant force and any error in the measurement of the pressure is considerably magnified. Moreover, it is possible that the manometer does not give an absolutely accurate measure of the pressure on account of the shape of the hole, although curves obtained with different holes are in quite good agreement. If the distance between the ball and the jet is either increased or decreased the pressure-distribution curves retain the same general appearance, the pressure on the lower part of the ball and therefore the resultant upward force on the ball being greater

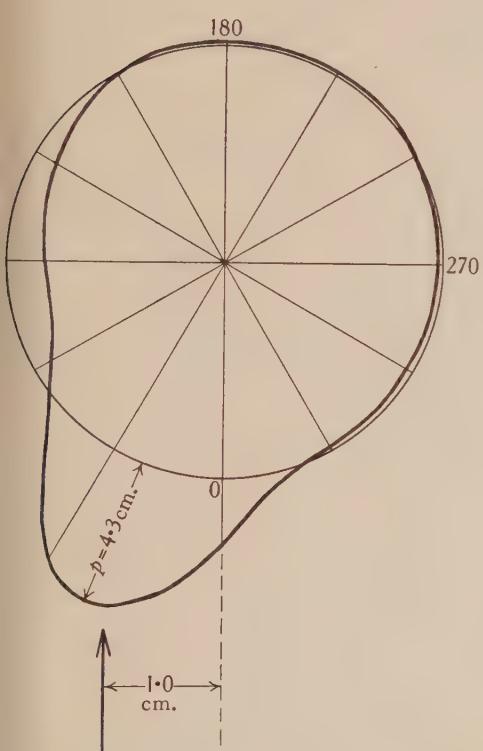


Figure 3. Pressure-distribution with the centre of the ball 1.0 cm. off the axis and 13.5 cm. above the jet.

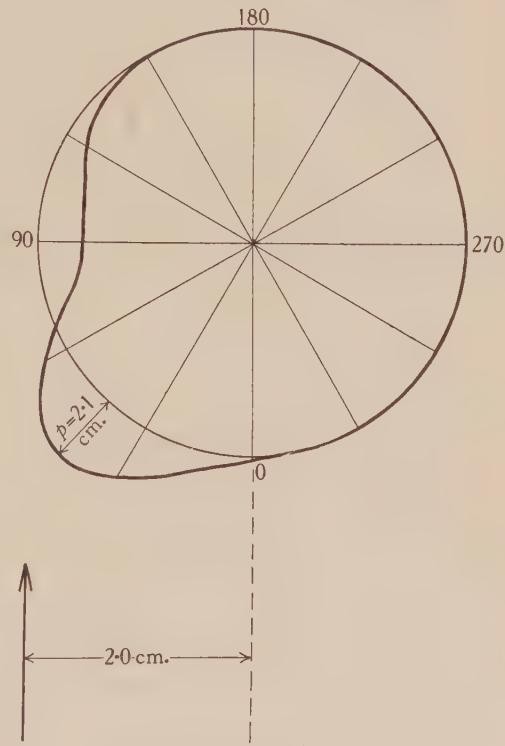


Figure 4. Pressure-distribution with the centre of the ball 2.0 cm. off the axis and 13.5 cm. above the jet.

the less the distance of the ball from the jet. Thus it is clear that a free ball stands at such a height above the jet that the resultant upward force exactly balances the weight of the ball.

The horizontal forces which tend to keep a free ball on the axis of the jet may be studied by obtaining the pressure-distribution curves when the jet is displaced to one side, in the vertical plane through the centre of the ball at right angles to the supporting tube. Curves obtained in this way when the jet is displaced 0.5, 1.0 and 2.0 cm. respectively are shown in figures 2, 3 and 4, the vertical height of the ball above the jet being 13.5 cm. as before. Owing to the unsymmetrical nature of the curves it is not possible to calculate the actual forces acting on the ball. It is quite clear, however, in each case that the side of the ball nearer to the axis of the

jet experiences a greater vacuum than the side farther from the jet, whence there is a horizontal force on the ball which tends to bring it back to its equilibrium position on the axis. Curves are not shown for displacements of the jet greater than 2·0 cm. but a slight vacuum of the order of 0·05 cm. of xylol can still be detected on the near side of the ball when the displacement is as great as 5·0 cm. From the curves it also appears that the resultant upward force on the ball is still considerable when the displacement is 0·5 cm. or even 1·0 cm., but has decreased considerably when the displacement is 2·0 cm. The curves suggest that owing to the reduction in the upward force the ball will fall if displaced by more than about 1·0 cm. from the axis of the jet. Experiments with the other two jets yielded similar pressure-distribution curves.

The above conclusions may be illustrated by a simple experiment in which a light cotton is attached to a ball either by wax or by being knotted through a small hole. If the ball is now supported by the air-jet and the cotton is pulled horizontally by the hand the ball becomes displaced and the horizontal restoring force on it is felt by the hand; but when the displacement exceeds about 1·0 cm. the ball falls, since the upward force is no longer sufficient to support it. That there is still a horizontal force acting on the ball when the displacement is much greater than 1·0 cm. can be shown, however, by suspending the ball with the cotton vertical and gradually bringing the air-jet nearer to the ball, the vertical distance between them being 13·5 cm. as before. When the axis of the jet is about 5·0 cm. from the centre of the ball the latter is drawn into the stream of air and lies approximately on the axis of the jet with the cotton inclined at an angle to the vertical.

AN X-RAY STUDY OF THE SUPERLATTICE IN CERTAIN ALLOYS

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ABSTRACT. Superstructures in the β phases of silver-zinc and gold-zinc alloys submitted to various heat treatments have been investigated. Whereas in the gold-zinc alloys the atoms were found in ordered arrangement both in quenched specimens and in specimens maintained at temperatures up to the melting points of the alloys, in the silver-zinc alloys ordered arrangement of atoms in the lattice was found only in quenched alloys. The results obtained are discussed in the light of the theory of order and disorder in alloys, put forward by Bragg and Williams.

§ I. INTRODUCTION

THE conditions under which superlattices are formed has been the subject of much theoretical and experimental research in recent years. Tammann⁽¹⁾ found that long annealing of an alloy produced a change in its resistance, and to explain this he suggested that the heat treatment had caused a change from a disorderly to an orderly distribution of atoms in the crystal lattice. Johansson and Linde⁽²⁾, examining the gold-copper alloy system by an X-ray method, found that such a rearrangement of atoms did occur. Observations carried out by Haughton and Payne⁽³⁾ and by Kurnakow and Ageew⁽⁴⁾ on the change in electrical resistance corroborated these results. Another notable contribution in this field is that of Bradley and Jay⁽⁵⁾, who made a comprehensive X-ray study of the problem as presented in the iron-aluminium alloy system.

The theoretical side of the problem has been studied by many workers, including Gorsky⁽⁶⁾, Borelius, Johansson and Linde⁽⁷⁾, Dehlinger and Graf⁽⁸⁾, Bragg and Williams⁽⁹⁾ and Bethe⁽¹⁰⁾. The general conceptions are similar in all treatments.

Bragg and Williams assume that at very low temperatures the equilibrium state of an alloy is one of perfect order. As the temperature rises the equilibrium degree of order decreases, slowly at first then more quickly, until complete disorder is reached at a certain critical temperature T_c , this temperature being characteristic of the alloy. Above T_c the alloy has a completely random distribution of atoms. By considering the time of relaxation of an alloy, that is the time of annealing required at any particular temperature to bring the alloy into equilibrium, these

authors are able to define two temperatures, T_q and T_a , such that alloys quenched from above T_q will always have the atomic distribution characteristic of the equilibrium condition at T_q , while any practicable time of annealing below T_a will fail to change the condition of the alloy. By quenching from any temperature between T_a and T_q the equilibrium condition at that temperature will be retained. According to the relative values of T_a , T_q , T_c and T_m (the melting point of the alloy), the following four possibilities arise.

Case 1. $T_c < T_a < T_q < T_m$. Although at low temperatures the equilibrium state has a certain degree of order, it will be impossible to obtain an alloy in this state since when cooling from the melt, the temperature T_a is reached while there is still complete disorder.

Case 2. $T_a < T_c < T_q < T_m$. Alloys with any degree of order equal to or less than that characteristic of T_a can be obtained by quenching from the appropriate temperature.

Case 3. $T_a < T_q < T_c < T_m$. In this case, although the equilibrium condition of the alloy between the temperature T_c and T_m is one of disorder, it will be impossible to retain this condition on quenching. All the alloys, whatever their thermal history, will have a certain degree of order at low temperatures.

Case 4. $T_a < T_q < T_m < T_c$. The equilibrium condition of alloys at all temperatures has a certain degree of order.

The experiments of Sykes⁽¹¹⁾ on the variation of specific heat in CuZn and FeAl alloys furnish evidence in support of the above theory.

In the course of a detailed study of the silver-zinc system of alloys, an account of which will appear elsewhere, superlattice lines were observed on certain spectrum photographs of the β alloys. It was resolved to examine these alloys more fully, both at low and at high temperatures, and to investigate similarly the analogous phase in the gold-zinc system. The possible existence of the temperature T_q , as suggested by Bragg and Williams, from above which it is impossible to retain the state of the alloy on quenching, could thus be investigated. Only alloys containing approximately 1 : 1 atomic ratio of constituents will be dealt with here. To obtain quantitative results, measurements of the intensities of the reflection lines are necessary, but these have not been made on the spectra which will be considered in this paper.

§ 2. THE β PHASE OF SILVER-ZINC

The β phase in the silver-zinc system extends at 300° c. from 49·4 to 54·3 atomic per cent of silver and widens as the temperature increases; at 600° c. it extends from 49·2 to 58·2 atomic per cent of silver. It possesses a body-centred cubic structure which changes to a close-packed hexagonal one below the transformation temperature which varies between 289° c. and 264° c. according to the composition of the alloy. The transformation differs from that of the β phase of copper-zinc where the body-centred cubic structure is retained below the transformation temperature.

Westgren and Phragmen⁽¹²⁾ obtained superlattice lines in spectrum photographs of a silver-zinc alloy containing 49·5 atomic per cent of silver taken at room temperature, but they did not pursue the matter further.

In the present investigation, the first spectrum photograph taken of an alloy which had been quenched from the pure β region was that of alloy 51·2,* annealed at 410° C. for 12 hr. The strongest lines in the spectrum were due to reflections from the planes, for which $Q^2 (\equiv h^2 + k^2 + l^2) = 2, 4, 6, 8, 10, 12$, of a cubic lattice, the parameter of which was about 3·15 Å. These are the lines to be expected from a body-centred cubic structure. In addition to these lines, there were present fainter reflections from planes of the same cubic lattice for which $Q^2 = 3, 5, 9, 11$. These last reflections showed that the centre and corners of the unit body-centred cubic cell were not structurally equivalent; there was a certain amount of segregation of the silver atoms to the corners and zinc atoms to the centres of the cubes (or vice versa). Another specimen from the pure β phase, alloy 53·0, annealed at 535° C. for 9 hr. and quenched, also gave superlattice lines.

Alloys quenched from the ($\alpha + \beta$) region also yielded spectra with superlattice lines, but the lines were fainter than those obtained with the pure phase alloys. The following are particulars of the heat treatments given to the alloys from the ($\alpha + \beta$) region which were investigated: (1) Alloy 55·2, annealed at 331° C. for 29 hr. and quenched. (2) Alloy 59·2, annealed at 535° C. for 9 hr. and quenched. (3) Alloy 58·0, annealed at 448° C. for 72 hr. and quenched.

The results of the measurements made on the photograph taken with alloy 59·2 using cobalt K_α radiation with an iron filter, are included in table I. The superlattice lines in the β phase were very faint but measurable and they yielded consistent values of the lattice parameter.

Table I

Strength of re- flection	Corrected arc (mm.)	log sin	Radia- tion	Reflection planes	α phase parameter (Å.)	Reflection planes	β phase parameter (Å.)
<i>m</i>	210·57	1·5879	K_x	(111)	3·998	—	—
<i>s</i>	208·03	1·6019	K_α	—	—	(110)	3·161
<i>f+</i>	198·76	1·6498	K_α	(200)	4·003	—	—
[<i>vf</i>]	<i>c.</i> 189	—	K_α	—	—	(111) (200)	<i>c.</i> 3·15 3·162
<i>m</i>	173·90	1·7522	K_α	—	—	(211)	—
<i>m</i>	158·98	1·8002	K_α	(220)	4·004	—	—
<i>s</i>	144·38	1·8403	K_x	—	—	(220)	3·162
<i>m+</i>	132·04	1·8691	K_α	(311)	4·007	—	—
<i>m</i>	123·03	1·8881	K_α	(222)	4·006	—	—
<i>s-</i>	115·45	1·9027	K_x	—	—	(300)	3·162
[<i>vf</i>]	100·0	1·9281	K_α	—	—	(221)	3·164
<i>s</i>	83·58	1·9506	K_α	(400)	4·006	(310)	3·167
[<i>vf</i>]	64·2	1·9712	K_α	—	—	(311)	3·167
<i>s</i>	43·21	1·9871	K_{α_1}	(331)	4·009	—	—
<i>s</i>	41·60	1·9880	K_{α_2}	(331)	4·008	—	—
<i>s</i>	38·41	1·9898	K_{α_1}	—	—	(222)	3·166
<i>s</i>	36·58	1·9908	K_{α_2}	—	—	(222)	3·165

* Alloy 51·2 means an alloy containing 51·2 atomic per cent of silver. This method of referring to the alloys will be adopted throughout the paper.

Difficulty was encountered in retaining the high temperature structures of alloys in the $(\beta + \gamma)$ region. Since the β component breaks down readily into the ζ phase, and the γ component gives a large number of spectral lines, it was impossible to tell with certainty whether the superlattice lines were present in photographs of quenched alloys in the $(\beta + \gamma)$ region.

The next step was to study the effect of quenching pure β -phase alloys from still higher temperatures. Three samples of alloy 53·0 were subjected respectively to the following heat treatments: (1) annealed at 650° c. for 30 min. and quenched, (2) annealed at 672° c. for 8 min. and quenched, (3) annealed at 691° c. for 7 min. and quenched. According to the equilibrium diagram published in the *International Critical Tables*, the alloy when annealed at 691° c. should be in the $(\beta + \text{liquid})$ region. The spectra obtained with the three specimens gave superlattice lines which appeared as strong as the lines obtained with specimens annealed at lower temperatures. The superlattice exists therefore up to the highest temperature at which the alloy's structure can be retained by quenching.

Evidence of the existence of a superstructure in all quenched alloys having been obtained, it remained to examine the alloys at high temperatures.

Alloy 53·0 was again used. It was annealed at 500° c. for 2 hr. in vacuo* and then a photograph was taken at 500° c., which occupied another period of 2 hr. No superlattice lines were observed but the lines from the body-centred cubic structure were also rather weak in the photograph so that the result was not conclusive. A similar result was obtained with another specimen of the alloy which had been annealed at 450° c. for 21 hr. A better photograph was obtained with the same alloy after a shorter period of annealing. When the specimen was kept at 400° c. for 15 min., before being exposed at this temperature for 1 hr. 45 min., the resulting spectrum contained strong well-defined lines from the body-centred cubic lattice but superlattice lines were absent. This experiment showed that the β phase was quickly formed at these temperatures.

It was feared that volatilization of the zinc might vitiate the results, although it had previously been ascertained that volatilization was slight in these alloys at temperatures below about 400° c. In order to reduce the effect as much as possible, the temperature of annealing was reduced to that just above the transformation temperature of β to ζ phase which at its maximum is about 289° c. Alloy 50·25 was accordingly annealed at 303° c. for 4 hr. 30 min. and then exposed at 303° c. for 1 hr. 30 min. Although in this photograph the contrast between the background and the spectral lines from the body-centred cubic planes was as good as that in the most successful photographs obtained with quenched alloys, there was no trace of superlattice lines.

It was considered possible that the equilibrium state of the alloys at this comparatively low temperature was one of order, but that the kinetic energy of the atoms might not be sufficient to cause much interchange of atoms. In this case if the β lattice, when first formed from the hexagonal lattice, had a random distri-

* All the specimens examined at high temperatures were maintained at these temperatures and exposed to the X-ray beam in vacuo.

bution of atoms, this distribution would remain random until the alloy was heated to a temperature considerably above 300°C . This possibility was disproved however by the following experiment. An alloy was heated below the transformation temperature for 2 to 3 hr. to ensure that the β lattice was destroyed. It was then annealed for 4 hr. between 295 and 303°C . and quenched, the latter temperature never being exceeded. The alloy when photographed gave good superlattice lines. The spectra are reproduced in figure 1. Hence an alloy in the pure β phase of silver-zinc quenched from a temperature of about 300°C , which is about 20°C . above the transformation temperature for the particular alloy examined, yielded strong superlattice lines, but the same alloy maintained at 300°C . yielded a spectrum in which there was no indication of a superstructure.

It was of interest to examine an alloy in the $(\alpha + \beta)$ region at elevated temperature. Accordingly alloy 55.1 which at 300°C . is in the $(\alpha + \beta)$ region, and situated nearer to the $(\alpha + \beta) - \beta$ than to the $\alpha - (\alpha + \beta)$ boundary, was studied.

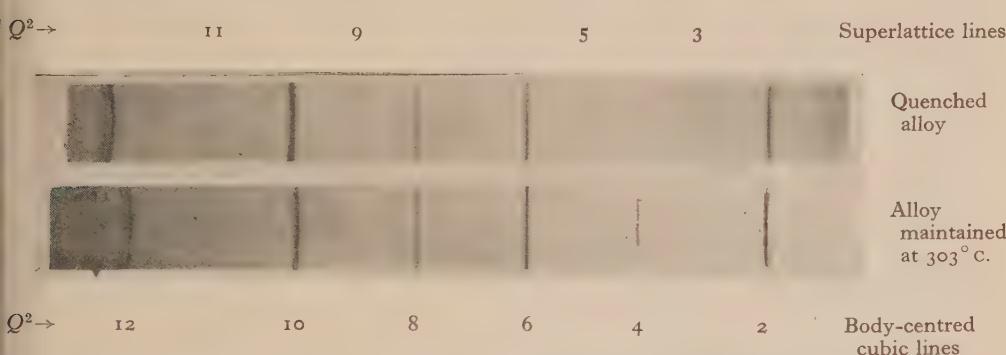


Figure 1. Superlattice lines in a quenched silver-zinc β phase alloy, but none at 303°C .

The alloy was mounted on the camera and maintained in vacuo at 300°C . for 3 hr. prior to the X-ray exposure at this temperature, which occupied a further period of 2 hr. The alloy was not a good reflector at high temperature and did not yield satisfactory lines. It was found necessary to increase the X-ray exposure to 4 hr. but even then the lines were not as intense as could be desired. Several photographs were taken but in each case the lines were very faint, and it was impossible from these photographs to state with certainty that the superlattice lines were absent. Improved conditions of exposure yielded better spectra, but no superlattice lines could be observed in the β -phase spectrum.

The lattice-dimensions of the component phases in a mixed region can be retained up to the melting point of the alloy, but the atoms may not be orderly distributed throughout the lattice at these temperatures. Order amongst the atoms in the lattice seems to set in at a comparatively low temperature. It would appear that a change in the size of the lattice entails a far greater disturbance of the atoms than does a change from disorder to order.

It is concluded from these experiments on silver-zinc alloys that

- All quenched pure β -phase alloys show superlattice lines. Therefore $T_q < T_c$

(case 3 or case 4); that is, a certain degree of order exists at all temperatures below T_q , the highest temperature at which the structure can be retained by quenching.

(ii) No pure β -phase alloys gave superlattice lines at high temperatures including 500, 450, 400 and 303° c. Hence $T_c < 303^\circ\text{c}$. and by (i) $T_q < T_c < 303^\circ\text{c}$., that is the highest temperature at which the property of ordered arrangement in the pure phase β lattice can be retained by quenching is less than some temperature T_c which is itself less than 303° c. The transformation temperature of β to ζ varies between 264 and 290° c. for alloys of different compositions.

(iii) Alloys in the $(\alpha + \beta)$ region, in which the β phase is saturated, when quenched from 331, 448 and 535° c. showed superlattice lines. Hence $T_q < T_c$ as in (i) above.

(iv) Alloys in the $(\alpha + \beta)$ region showed no β -phase superlattice lines at high temperatures. In this case T_q is less than the lowest temperature at which the alloy can be examined above the transformation temperature. But the size of the lattice can be retained by careful quenching from temperatures up to 600° c., and without much difficulty up to 450° c. There is therefore a different temperature T_q for the two properties, (a) the size of the lattice, and (b) the ordered distribution of the atoms.

If the atomic distribution were entirely random at high temperatures, it would be expected that the beginning of the ordering process would be slow, as initially there would be no right and wrong positions, as they may be called, for the atoms, but this does not appear to be the case. To explain the results obtained with quenched and heated specimens of silver-zinc alloys, it could be assumed either (1) that the silver and zinc atoms are able at high temperatures to interchange positions rapidly resulting in a random distribution and that this random interchange persists until a comparatively low temperature is reached, when order sets in, or (2) that the structure at high temperature is not entirely random but possesses a certain degree of order of a type which is not revealed by X-ray examination. For instance, the silver and zinc atoms may be paired off, that is, the movement of a certain silver atom may be closely associated with that of a certain zinc atom. This would require, as in J. J. Thomson's dipole theory, entities similar to dipoles (polarized molecules), the axes of which are oriented at random at the higher temperatures within the limitations set by the crystal structure but tend to the same orientation at some lower temperature when the disturbance due to the thermal vibration becomes small compared with that due to the forces of the crystal lattice.

Although the structure does not possess a superlattice at high temperatures, the readjustment of the atoms required to produce such a superlattice may be small compared with that required to change the size of the lattice or to change the structure of the crystal. On quenching, the cooling is rapid enough to prevent the pure β -phase alloys from changing into the hexagonal ζ structure, but at some temperature in the cooling process the silver and zinc atoms settle into positions of least potential energy in a body-centred cubic lattice. The critical temperature T_c at which this rearrangement of the atoms begins may be anything below that of quenching, and it may be well below the temperature at which transformation

to the ζ phase normally takes place. The temperature T_c is certainly below 303°C . in the pure β phase as is shown under (ii) above.

Weerts⁽¹³⁾ also found that superlattice lines obtained with quenched alloys were absent when the alloys were examined at high temperatures. He sought to explain this by suggesting that the atoms in the β phase were distributed at random in the lattice but that they became ordered on quenching.

§ 3. THE β PHASE OF GOLD-ZINC

The β phase of gold-zinc, like that of silver-zinc, possesses a body-centred cubic structure. According to the accepted equilibrium diagram of this system, the β phase of gold-zinc differs from the β phase of silver-zinc in that the former does not transform to another phase at low temperature. Westgren and Phragmen⁽¹²⁾ obtained superlattice lines with a gold-zinc β -phase alloy at room temperature.

For the present investigation a gold-zinc alloy was prepared by melting a mixture of gold and zinc filings in an evacuated silica tube, the mixture being well shaken while it was molten. Specimens of the alloy in powder form were given the following heat treatments before being photographed at room temperature. Alloy 50.8 containing 50.8 atomic per cent of gold: (1) annealed at 250°C . for 76 hr. and quenched; (2) annealed at 603°C . for 6 hr. and quenched; (3) annealed at 720°C . for 18 min. and quenched.

All three spectra contained strong superlattice lines showing that this β -phase alloy consisted of two interpenetrating simple cubic lattices, one of gold and the other of zinc atoms, the corner of a unit cell of the one being at the centre of a unit cell of the other. The spectrum obtained after heat treatment (3) above is shown at the top of figure 2. The equilibrium diagram of the gold-zinc system gives 726°C . as the melting point of a β -phase alloy. The superstructure is thus present in alloys quenched from all temperatures up to within a few degrees of the melting point.

Five high-temperature photographs of the alloy were taken; the results are shown in the table:

Temperature (° C.)	Remarks
400	Superlattice lines present.
528	Superlattice lines present but also a trace of α -phase lines showing volatilization of zinc.
560	Distinct superlattice lines but a fair amount of α phase present
577	Faint superlattice lines, which appear to be fainter in relation to the body-centred cubic lines than are those in photographs taken at lower temperatures. The α -phase lines had increased in intensity.
640	No trace of β -phase lines. The only lines present were from a face centred cubic lattice and the doublets were well resolved. All the zinc had volatilized before the exposure was started, leaving gold.

The photographs are reproduced in figure 2. The spectra show that the superlattice exists up to a temperature of 577°C . at least, though the photograph taken

at this temperature suggests that it may disappear at still higher temperatures. If this be so, the photographs obtained with quenched alloys indicate that the equilibrium state at these high temperatures cannot be retained by quenching. But there may be some cause additional to the heat motion of the atoms to account for the faintness of the superlattice lines at the higher temperatures.

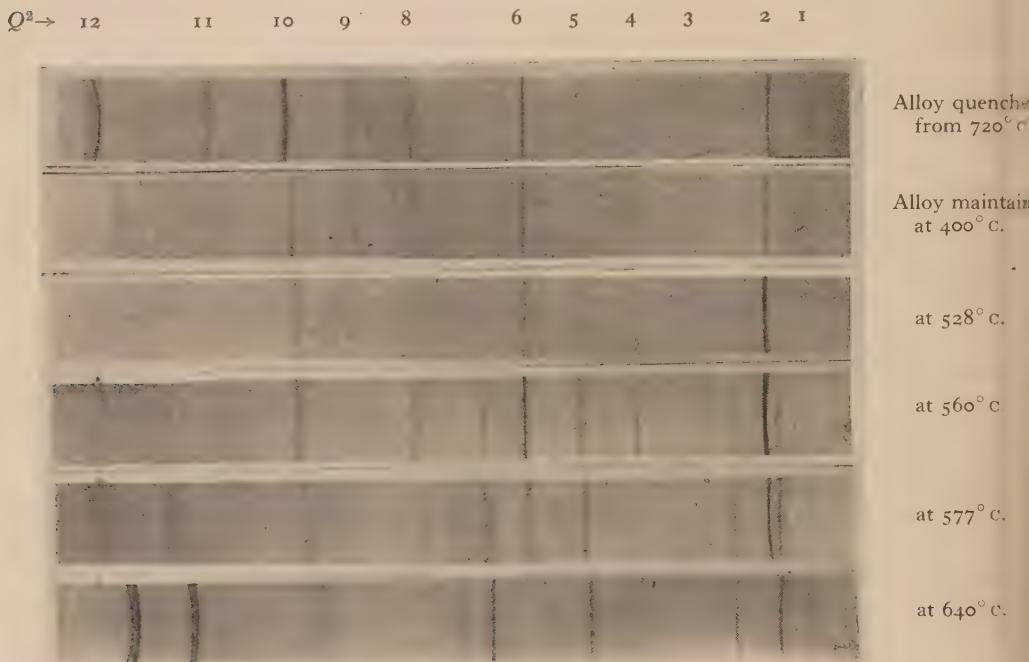


Figure 2. Superlattice lines in a quenched gold-zinc β -phase alloy and in the same alloy when maintained at high temperatures.

After this work had been completed a reference to an investigation by Soldau⁽¹⁴⁾ was found. In his paper it is recorded that superlattice lines were obtained with β -phase gold-zinc alloys at temperatures up to 550°C .

The results of the work on β -phase gold-zinc alloys may be summarized in the following statement. In alloys quenched from temperatures up to the melting point a superstructure is present. This superstructure is also present at temperatures ranging from 400 to 577°C . and possibly at higher temperatures up to the melting points of the alloys.

§ 4. CONCLUSIONS

The behaviour of a 50-atomic-per-cent alloy of silver-zinc under various heat treatments differs from that of a 50-atomic-per-cent alloy of gold-zinc subjected to similar heat treatment. Whereas with the latter the atoms are orderly arranged both in quenched specimens and specimens maintained at temperatures in the range extending from room temperature to the neighbourhood of the melting point of the alloy, in the former an orderly arrangement of atoms in the lattice was

found only in quenched alloys. A random distribution of atoms in the lattice was found in alloys maintained at temperatures between 300°C . and the melting points of the silver-zinc alloys. Below about 300°C . a transformation of the body-centred-cubic β phase to the hexagonal ζ phase takes place. No such change of structure has been observed in this region for gold-zinc alloys. This difference between the phase fields in this region of composition in the two alloy systems may account to some measure for the difference in behaviour between the alloys.

Both alloys may be considered under cases (3) and (4) of Bragg and Williams mentioned above. In the gold-zinc alloys the critical temperature T_c may be higher than the melting point T_m , and T_q may be as high as the melting point. This alloy would therefore come under case (4). But the present investigation does not enable a definite distinction to be made between cases (3) and (4), for volatilization of zinc made it impossible to ascertain the highest temperature at which the superstructure existed. Quenched alloys, although they showed the presence of superstructure up to the highest temperature of quenching, which was close to the melting point of the alloy in each case, did not supply the information required as to the relative values of T_q and T_c .

With the silver-zinc alloys which were maintained at elevated temperatures it was possible to show quite definitely that for these alloys $T_q < T_c < 300^{\circ}\text{C}$. That is, a pure β -phase alloy had a critical temperature close to the transformation temperature, and T_q may be at or below the transformation temperature.

It is suggested that there may be in alloys at high temperature some type of order which cannot be detected by X-rays. This suggestion is based on the behaviour of the β phase in simple and duplex regions.

The present investigation is to be regarded as preliminary to a more detailed examination of these and other alloys which is now in progress.

§ 5. ACKNOWLEDGEMENT

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THE RELATIVE LUMINOSITY OF RADIATION AT WAVE-LENGTHS 5780 AND 5461 A. FOR THE AVERAGE PHOTOMETRIC OBSERVER

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ABSTRACT. The relative luminosity of radiation of wave-lengths 5780 and 5461 A. has been determined for sixteen observers whose mean Y/B ratio was 1.003, using the Guild flicker photometer with 2° field, and a field illumination of 25 to 30 lux. The corresponding relative energy measurements were made with a calibrated emission type photocell. The source of light was a high-pressure mercury discharge lamp with selective colour filters to isolate the two spectrum lines concerned. The results show good agreement with the value based on the luminosity factors adopted internationally in 1924 by the Commission Internationale de l'Éclairage. The paper includes details of the filters used, the method of calibration of the photocell, and investigations on the linearity of response and possible colour-selectivity of the thermopile used for the calibration. The question of the influence of field-size on the results is examined and discussed also.

§ 1. INTRODUCTION

In 1924 the Commission Internationale de l'Éclairage officially adopted a table⁽¹⁾ of values of the relative visibility or luminosity factor based on the average values for a large number of colour-normal observers, previously determined by a number of investigators, notably Gibson and Tyndall. The conditions and results of these determinations are summarized by Gibson⁽²⁾. These C.I.E. standard luminosity factors form the fundamental basis of the colour test using the yellow/blue (or Y/B) ratio for the classification of the colour properties of photometric observers⁽³⁾, and also the basis of all methods of heterochromatic photometry using minimum colour-difference and a small field, such as the flicker method and the use of colour-match filters for direct comparison. More recently, however, Arndt⁽⁴⁾ and Dresler⁽⁵⁾, and Federov and Federova⁽⁶⁾ have re-examined the validity of the standard luminosity curve.

Federov and Federova used the cascade method with 1.5° field, full light-adaptation and daylight illumination in the photometer room. Their determinations were made throughout the spectrum, but the values deduced from their results for the relative luminosities at 5780 and 5461 A. are given as 1.028 and 1.095 for the two investigators respectively.

Arndt and Dresler both used the powerful sources of monochromatic light now available in the form of electric discharge lamps. They used a Bechstein flicker

photometer for visual comparison of different spectrum lines, and a calibrated selenium rectifier photocell as intermediary for the necessary relative energy determinations. The field size of the flicker photometer was $1\cdot5^\circ$ or less, and a bright surround field was used to obtain light adaptation. Arndt determined the relative luminosity for the yellow and green mercury lines, obtaining a value $K_{5780} : K_{5461} = 1\cdot035$ for the average of some 50 observers, while Dresler extended the wave-length range to include the sodium yellow doublet, obtaining $K_{5893} : K_{5461} = 0\cdot94$ for the average of 34 observers. These values were obtained for a field illumination of about 30 lux.

None of these four investigators gives information as to the Y/B ratios of the observers concerned in the measurements, but all are agreed in stressing the importance of reducing the field-size to about 1° in order to ensure pure cone-vision. They infer that this reduction is mainly responsible for the difference between their results and the figures derived from the C.I.E. standard values, which are $K_{5780} : K_{5461} = 0\cdot899$ and $K_{5893} : K_{5461} = 0\cdot781$, the third significant figure here depending, within a range of 3 or 4, on the method of interpolation used.

By examining the data summarized by Gibson⁽²⁾, one can also obtain the values shown in table 1 on the basis of the determinations of relative luminosity made by the investigators whose work was considered in the derivation of the C.I.E. standard table. With some exceptions the field illumination used by these investigators was of the order of 25 lux. The pupil conditions at the eye itself were not exactly specified.

Table 1

Investigators	Field-size	$K_{5780} : K_{5461}$
Hyde, Forsythe and Cady	8°	0·887
Gibson and Tyndall	3°	0·894
Ives-Nutting	2°	0·910
Coblentz and Emerson	2°	0·931

Here the differences among the figures in the last column are considerably smaller than that between the figures obtained by Arndt, and Federov and Federova, and that based on the C.I.E. standard luminosity factors. This is so despite the fact that rod vision would be operative to an appreciable extent in the 8° field used by Hyde, Forsythe and Cady, and the 3° field of Gibson and Tyndall, but relatively inappreciable for the 2° field employed in the other two cases included in table 1.

In view, therefore, of the departures of the more recently determined values from the C.I.E. standard luminosity factors, it is of importance to examine again the validity of the latter under the experimental conditions to which they most nearly apply. Although not specifically laid down, these may be stated as follows: Field-size, 2° with minimum colour-difference; apparent field-brightness, 25 to 30 equivalent lux; surround field of similar brightness, and of size 20 to 30° ; normal unrestricted pupil diameter; darkened photometer room.

It should be noticed here that the value to the photometrist of the C.I.E. standard factors lies in their reproducibility under set conditions, suitable for general photometric purposes, rather than in any specific visual characteristic which they may represent. They are intended to define, under the specified conditions, a photometric scale adequately representative of possible observers.

The present paper describes a series of measurements on the ratio $K_{5780} : K_{5461}$ on the same general lines as Arndt's investigation, but using a Guild flicker photometer⁽⁶⁾ for the visual work, and a calibrated vacuum emission photocell for the measurements of relative energy. It also describes the tests made to ensure the accuracy of the calibration of the cell, and to arrive at as complete a knowledge of its characteristics as possible. Sixteen colour-normal observers took part, and their Y/B ratios are given in the table of results. A further examination was also made of the influence of a reduction in field-size from 2° to 1° , twelve observers taking part.

§ 2. PRINCIPLES OF THE METHOD

A Guild flicker photometer G , figure 1, and a photoelectric photometer P , using the calibrated photocell, were mounted one above the other, as close together as possible, in a fixed position on a photometer bench. Beyond the end of the bench

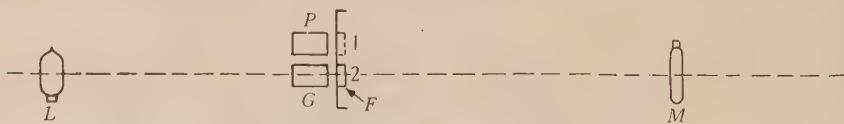


Figure 1. Photometric system.

a 250-w. mercury discharge lamp M was mounted at a fixed distance from the photometers. Light from M was incident on the photocell in P and also on the rotating vanes of G . A tungsten lamp L of the uniplanar-filament type was movable on the bench to provide the comparison source for measurements made with G , and illuminated the fixed test surface of G via the usual mirror contained in G . Any selectivity in this mirror therefore affected only the constant comparison source, and introduced no error in the comparative measurements of the radiation from M . The test surfaces of G were freshly smoked with an adequate thickness of magnesium oxide, whose colour-selectivity is known to be negligible^(8,9).

The flicker photometer had a large exit pupil, a 2° field, and a surrounding field set to a brightness slightly lower than that of the flicker spot. The desired spectrum line of M was isolated by a filter located at F and movable in a slide S so as to cover P or G at will.

The sequence of measurements was as follows: (1) Filter for green line in position 1; reading on P . (2) Filter for green line in position 2; ten visual observations by each of two observers on G , with movable comparison lamp. (3) Filter for green line in position 1; check reading on P . (4) Filter for yellow line in

position 1; reading on P . (5) Filter for yellow line in position 2; visual observations on G . (6) Filter for yellow line in position 1; check reading on P . We then have

$$\frac{K_{5780}}{K_{5461}} = \frac{(5)}{(2)} \times \frac{\text{mean of (1) and (3)}}{\text{mean of (4) and (6)}} \times \frac{S_{5780}}{S_{5461}},$$

where S_{5780}/S_{5461} is the ratio of the sensitivities of the photocell per unit incident energy of the wave-lengths concerned.

The above sequence of measurements was repeated for other pairs of observers, and for the same pairs on different occasions. Its shortness, in time, avoided the effect of possible changes in transmission of the filters due to changes in temperature, and also provided frequent checks on the constancy of M by means of the high-precision photoelectric readings. M was operated on alternating current, the value of this current being kept constant, and the distances of M and L from the photometers were arranged to give an illumination at the photometer within the range 25 to 35 lux.

One point assumed in the above method is that the composition of the radiation from M falling on P is identical with that incident on G . There seems no reason to doubt the validity of this assumption in view of the relatively large distance between M and G (over $1\frac{1}{2}$ m.).

§ 3. CALIBRATION OF THE PHOTOCELL

The photocell used was a vacuum cell of the Osram KMV 6 type operated at a voltage giving approximate saturation. In order to avoid trouble due to uncertainty of light-distribution on the cathode it was calibrated and used throughout in conjunction with a disc of Ilford diffusing medium mounted at a short fixed distance in front of the cell. All the figures given for relative colour-sensitivity of the cell therefore include any selectivity in this diffuser.

The first spectral calibration was carried out in November 1936, on the spectrophotometer apparatus described by Preston and Cuckow⁽¹⁰⁾, with a tungsten-filament lamp as light-source, and a linear thermopile in the telescope slit to determine the relative transmitted energy at various wave-lengths. The wave-length calibration of the spectrometer was carefully checked beforehand by means of the iron and copper arcs. Precautions were also taken to ascertain whether the small fraction of radiation escaping between the targets of the thermopile (and therefore the percentage falling on the thermopile) was reasonably constant throughout the spectrum. Photoelectric measurements showed that this was so. Further precautions were taken to eliminate the effect of stray light in the spectrometer by the use of appropriate colour filters to assist in purifying the light. A result

$$S_{5780} : S_{5461} = 0.688$$

was obtained.

By a similar method, but with a 125-w. extra-high-pressure mercury tube as source of light in conjunction with the spectrometer and the actual photoelectric photometer used subsequently, a value of 0.709 was obtained in the same month.

Both methods were repeated after the present work (August 1937) and values 0.698 and 0.715 respectively were obtained. The photocell thus appeared to be sufficiently stable, and a final mean value of $S_{5780} : S_{5461} = 0.702$ was adopted, the probable error on this figure being $\pm 1\frac{1}{2}$ per cent.

§ 4. {ILLUMINATION, CURRENT} CHARACTERISTIC OF THE PHOTOCELL

The {illumination, current} characteristic of the cell was checked by the methods described by Preston and McDermott⁽¹¹⁾ and Preston and Cuckow⁽¹⁰⁾ and was found to be linear within a few parts in 10,000 over the range of photo-currents and wave-lengths applicable to the present investigation.

§ 5. CHARACTERISTICS OF THE THERMOPILE

The use of the thermopile for measurements of relative energy involves two assumptions: first, that the thermal e.m.f. developed is proportional to the absorbed energy (of constant wave-length) over the range of measurement; and secondly, that the absorbed energy is a constant percentage of the incident energy over the range of wave-lengths concerned, i.e. the thermopile is non-selective.

The first assumption was examined by comparison of the readings of the thermopile with those of the photocell itself, when the two were exposed in turn to varying amounts of radiation of constant wave-length. The characteristic of the thermopile was not found to deviate from that of the photocell by more than a few parts in 10,000 and may therefore be regarded as linear to an accuracy well within that required.

The second assumption was examined in two ways. In the first, the thermopile targets were strongly illuminated by a steady mercury lamp and an image of them was focused on the collimator slit of the photoelectric spectrophotometer. The ratio of the readings given by the yellow and green mercury lines was noted, the telescope slit being wide enough to accept the entire image in each case. The thermopile was then replaced by a fresh surface of magnesium oxide and the ratio was again noted. The difference between these ratios indicates the difference between the reflection factors of the targets for the light of the two mercury lines, assuming the magnesium oxide to be non-selective. With care to avoid conditions of specular reflection a difference of about 5 per cent was recorded. Since, however, the absolute reflection factor of the targets was found by the same experiment to be approximately 4 per cent, this difference in reflection factor corresponds to a difference in absorption factor of only about 0.2 per cent as between the two wave-lengths considered. This is negligible for the present purpose.

In the second method a direct calibration of the photocell was attempted, the spectrometer set-up being used. The collimator slit was directly illuminated by a tungsten-filament lamp of known colour temperature and the ratio of the readings was noted when the wave-length was set successively to 5780 and 5461 Å., constant slit-widths being used. Given the distribution of relative energy of the source, the

dispersion correction of the spectrometer, and its relative optical transmission at the two wave-lengths, the relative transmitted energy could be calculated and the relative sensitivity of the photocell obtained. Unfortunately the optical transmission of the spectrometer was not known, but it was assumed to be the same for the two spectrum lines, in view of their narrow separation. With this assumption, the value of $S_{5780} : S_{5461}$ obtained differed from the mean of the other determinations by only 1 part in 700, and the method may therefore be regarded as confirming the correctness of this mean value.

§ 6. THE COLOUR FILTERS

The filters used to isolate the lines were: (1) For 5780 Å., a Chance-Parsons deep orange glass No. 3 of thickness 3.68 mm. together with 1 cm. of a 0.3-M. aqueous solution* of cupric chloride. (2) For 5461 Å., a Chance didymium glass, of thickness 10.00 mm., with Chance-Parsons green glass no. 5, of thickness 2.78 mm. All the components, including the liquid-cell, were optically worked. The spectral transmission curves are shown in figure 2, while the transmission value for the principal mercury lines are shown in table 2.

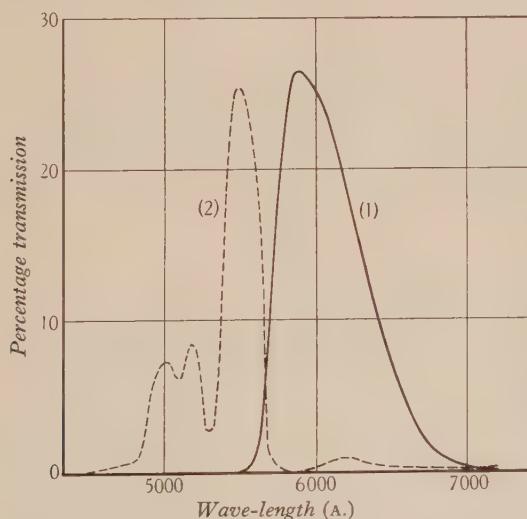


Figure 2. Spectral transmission of filters (1) and (2).

Table 2

λ (Å.)	T (per cent)	
	(1)	(2)
5780	21.74	0.04
5461	0	17.9
4916	0	4.8
4358	0	0
4046	0	0

* M stands for the molecular weight in grams per litre of solution.

The combination (1) transmits a certain amount of the continuous background at the red end of the spectrum of the mercury discharge lamp, but calculation shows that this amount is unimportant in the case of the 250-w. lamp used. The calculated purity of the radiation transmitted by the filters, based on relative energy values given by Taylor and Kerr⁽¹²⁾, is in both cases well over 99 per cent.

It is to be noted that both filter combinations have sharp cut-offs of the type showing temperature effects. This necessitated short cycles of measurements, as described in § 2.

§ 7. USE OF ALTERNATING CURRENT FOR THE LIGHT-SOURCE

The discharge lamp *M* was operated throughout the main investigation on alternating current, for which it was designed. The object was to preserve the steadiness and constancy of the lamp as well as possible for the considerable time during which it was alight. On the other hand, stroboscopic effects due to this fact were not entirely absent from the field of the flicker photometer. It was therefore thought desirable to ascertain whether the photometric balance was affected thereby in any systematic way. Results of previous tests in the Photometry Division of the National Physical Laboratory were available, and revealed no systematic difference. In the present case, however, a further experimental test was made by four observers under conditions identical with those of the main investigation, and this again revealed no systematic difference between results obtained with *M* operated on alternating and direct-current supplies respectively. The actual mean observed difference was $\frac{1}{2}$ per cent, which is well within the limits of experimental error.

§ 8. EFFECT OF FIELD-SIZE IN THE FLICKER PHOTOMETER

In view of the importance assigned by various authors to the matter of field-size it was considered desirable to investigate whether a reduction from the normal 2° field of the Guild flicker photometer to 1° would influence the results by a more complete elimination of rod vision. A removable stop was therefore made to fit over the 2° aperture of the photometer, to reduce the field-size to 1° , forming at the same time a continuation of the illuminated surrounding field provided in the instrument. In order to obtain the highest precision in the comparison of results obtained for the two field-sizes respectively the lamp *M* was operated on direct current. A photometric comparison of the two filtered radiations from *M* was then carried out using the flicker photometer, each observer using the 1 and 2° fields successively. Observers worked in pairs to avoid fatigue. No attempt was made to obtain any absolute values of $K_{5780} : K_{5461}$ from this subsidiary investigation, so that photoelectric readings were omitted. In other respects, however, the conditions were identical with those under which the results in § 9 were obtained.

The results are in table 3, the figure given being the ratio of the two figures proportional to $K_{5780} : K_{5461}$ obtained by each observer using field-sizes of 1 and 2° respectively.

Table 3

Observer	$\frac{[K_{5780} : K_{5461}]_1}{[K_{5780} : K_{5461}]_2}$	Observer	$\frac{[K_{5780} : K_{5461}]_1}{[K_{5780} : K_{5461}]_2}$
HFM	0.990	FJCB	1.021
GEVL	0.963	JSP	0.944
GCC	0.999	BJO	0.982
HRS	0.979	GWGS	0.973
LHMCD	0.997	WB	0.991
FMH	0.975	HB	0.964
Mean ratio = 0.980			

It is seen from the table that all the observers except one obtain a lower figure for the yellow/green luminosity ratio when using the smaller field. As a whole the results appear to show definitely a systematic field-size effect. The amount of the effect is, however, small, the mean change in relative luminosity being 2.0 per cent for the 12 observers. This change is hardly greater than the estimated experimental error.

§ 9. FINAL RESULTS

The values of $K_{5780} : K_{5461}$ obtained by the sixteen observers, together with the Y/B ratio of each, are set out in table 4.

Table 4

Observer	Y/B ratio	K_{5780}/K_{5461} observed	Mean K_{5780}/K_{5461}
FMH	0.981	0.838, 0.854, 0.844	0.845
GEVL	1.030	0.896, 0.894	0.895
HB	1.052	0.897, 0.906	0.902
LHMCD	0.938	0.831, 0.855	0.843
WB	1.032	0.911, 0.964	0.938
JSP	0.963	0.872, 0.882	0.877
HFM	0.936	0.834	0.834
JWTW	1.039	0.910, 0.958	0.934
BHC	0.977	0.921, 0.867	0.894
THH	1.062	1.026, 0.974	1.000
FJCB	1.065	0.907, 0.951	0.929
HRS	0.979	0.863, 0.913	0.888
GCC	0.970	0.925, 0.912	0.919
CD	0.930	0.891, 0.838	0.865
GWGS	1.089	1.010, 0.984	0.997
BJO	1.010	0.874, 0.905	0.890
Mean	1.003		0.903

Colour temperature of comparison lamp, 2230° K. approximately; field-size of flicker photometer, 2° ; field-brightness, 25 to 35 equivalent lux; an illuminated white surrounding field was employed in all cases. The photometer room was darkened.

§ 10. DISCUSSION OF RESULTS

Examination of the figures in column 3 of table 4 shows appreciable differences between the results obtained by the same observer on different occasions. These differences may be due to experimental error, to actual changes in the colour-sensitivity of the observer, or to both. The reproducibility of a single determination is assessed at $2\frac{1}{2}$ per cent, apart from any systematic error arising from the value used for $S_{5780} : S_{5461}$, so that in almost all cases the groups of figures in column 3 lie within the limits of error. This does not, however, necessarily exclude the possibility of changes in colour-sensitivity of individual observers.

In column 4 are given the individual mean values of $K_{5780} : K_{5461}$ and at the foot of the column the final mean value of 0.903. The value derived from the C.I.E. agreed curve is 0.899. The present results therefore show excellent agreement with

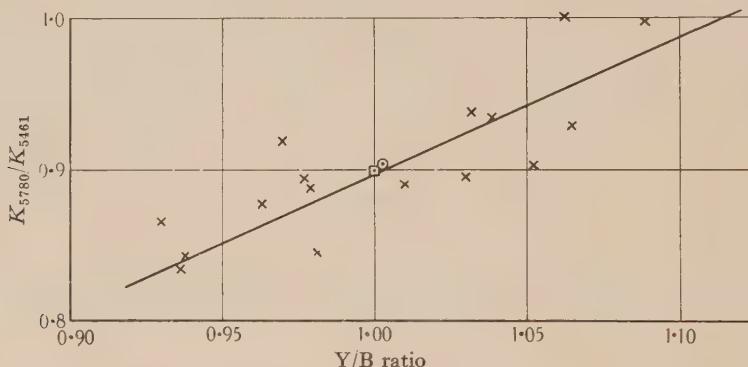


Figure 3. Relation between $K_{5780} : K_{5461}$ and the Y/B ratio. ◎, centroid of observed values; □, C.I.E. standard eye; x, observed points.

the C.I.E. standard average eye, on the assumption that the mean readings of sixteen observers having a mean Y/B ratio of 1.003 are sufficiently representative.

If now the result of § 8 is used to reduce the mean observed value to a figure corresponding to the 1° field condition, the figure of 0.885 is obtained. This is in conflict with the inference to be drawn from the work of the other investigators mentioned, which is that a higher value of $K_{5780} : K_{5461}$ might be expected for the small-field condition.

A close systematic relationship between the quantity $K_{5780} : K_{5461}$ for each observer and his Y/B ratio is not necessarily to be expected. Figure 3 shows, however, that there is some such relationship when the results are considered as a whole. In this diagram individual mean values of the observed luminosity ratios are plotted against the Y/B ratios of the corresponding observers. The best straight line through the plotted points, obtained by the method of least squares, is also shown. The centroid of the experimental points and also the point corresponding to the C.I.E. standard observer are also plotted. These last two points lie close to each other and to the straight line which best represents the relationship between the two variables considered.

Further examination of this relationship is not within the scope of this paper, but it may be suggested here that it may possibly be explained on the basis of a bodily displacement of some definite luminosity curve towards shorter and longer wave-lengths, without change of shape.

It is next to be noted that the mean Y/B ratio of the sixteen observers employed, and chosen at random, was 1.003. Other workers in various countries have measured the Y/B ratios of larger groups of observers under similar experimental conditions and have obtained overall mean values very close to unity. This in itself is additional confirmation of the correctness of the standard luminosity curve as representative of the average human eye, since it is on the basis of the standard curve that the calculated total transmissions of the two filters employed in the Y/B ratio test have equal values.

§ 11. CONCLUSIONS

The results of the foregoing investigation may now be summarized thus:

(1) With the Guild flicker photometer, a 2° field, a field-brightness of 25 to 30 equivalent lux, a surround field of similar brightness and full eye-pupil in a dark photometer room, the mean value of $K_{5780}:K_{5461}$, i.e. (luminosity for 5780 Å.)/(luminosity for 5461 Å.) was found to be 0.90, for sixteen observers having a mean Y/B ratio of 1.003. This value agrees, within the limits of experimental error, with the ratio of 0.90 based on the C.I.E. standard luminosity values.

(2) Under the above conditions the field-size effect below 2° is detectable but small, and probably of the same order as the experimental error.

(3) The luminosity ratios for different observers show a general systematic relationship with their Y/B ratios.

The following results were incidental to the main investigation: (a) With suitable sector speeds no systematic errors due to stroboscopic effects were observed in the flicker photometry of intermittent light-sources of periodicity 100 c./sec. (b) The colour selectivity of a thermopile smoked with camphor black is negligible for the wave-length range considered. (c) Indirect support is lent to the correctness of the C.I.E. standard luminosity data by the fact that the mean Y/B ratio of the sixteen observers chosen at random was 1.003. A bodily shift of the standard C.I.E. curve as suggested by Arndt and Dresler (*loc. cit.*) in explanation of their results, would involve a change in this mean Y/B ratio to a value of approximately 1.10.

A more complete investigation, applied to a large number of lines distributed through the spectrum, is desirable and one has already been begun.

§ 12. ACKNOWLEDGEMENTS

The author's thanks are expressed to Mr H. Buckley for much helpful discussion and advice with regard to the visual measurements, and to his colleagues Mr L. H. McDermott, Mr F. M. Hale, and others of the Photometry Division, National Physical Laboratory, who assisted with the measurements.

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THE PURIFICATION AND MAGNETIC PROPERTIES OF MERCURY

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MS. received 7 February 1938

ABSTRACT. Differences between the magnetic properties of several specimens of mercury prepared by the Hulett method were removed by subsequently heating the mercury in vacuo at 260° c. for some time. The temperature variation of the mass susceptibility of mercury so treated was measured and the results are discussed with reference to a theory given by Stoner.

IT is generally accepted that the best method of purifying mercury is that devised by Hulett⁽¹⁾ in which the metal, initially treated by the usual washing, high temperature distillation, and bubbling with air for many hours, is subsequently filtered and distilled in a stream of air at a pressure of about 2 cm. It is also generally assumed that mercury so prepared does not contain occluded gas, although Richards and Wilson⁽²⁾ reported that they had reason to fear that it contained a trace of oxygen; unfortunately, they gave no experimental evidence in support of their statement.

In the course of experiments⁽³⁾ on the magnetic properties of amalgams certain small differences were observed in the magnetic properties of mercury specimens which had been subjected to different temperature treatments, and were particularly noticeable in determinations of the temperature variation of mass susceptibility. It was therefore thought worth while to prepare mercury specimens by the Hulett method under different pressures of air during distillation and to find the mass susceptibilities of these specimens over the temperature range 16 to 300° c. The susceptibility-measurements were made by the Gouy method upon test specimens of mercury under the following conditions: (a) the mercury was placed in a degassed pyrex tube evacuated by means of a Hyvac pump and sealed; (b) the tube with the same mercury was again connected to the Hyvac pump and the liquid was boiled in a furnace maintained at 260° c. for 2 hr., after which the tube was sealed, one pyrex tube being used for as many specimens as possible to facilitate comparison.

In measurements following treatment (a), the curve of mass susceptibility against temperature always showed a discontinuity in the region of 140 to 180° c. In the case of specimens prepared in air at a pressure of 2 cm. or less, the diamagnetic susceptibility at room temperature for the (a) experiments was always less than that for the (b) experiments, and, even in the (a) experiments themselves, there

was a very slight increase in the room temperature value of the diamagnetic susceptibility after the specimen had been heated to 300° C. The nature of the discontinuity is shown in the figure.

One specimen was specially prepared in a stream of air at the relatively high pressure of 5 cm. and, while it showed a discontinuity at about 180° C., the values of the diamagnetic susceptibility at the lower temperatures in experiments (*a*) were definitely higher than those obtained in experiments (*b*), in marked contrast to the results with lower pressure preparations. The changes produced by boiling the mercury are small and rarely exceed 5 parts in 1000; it is difficult to follow them with precision. It is, however, strongly recommended, on the basis of the experiments described above, that mercury prepared by the Hulett method be subsequently boiled in an evacuated vessel before use.

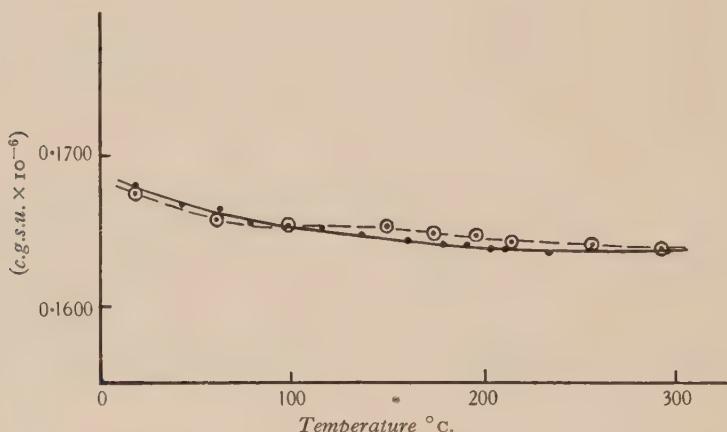


Figure 1. Mass susceptibility of mercury as a function of temperature; \odot , before boiling in vacuo; \bullet , after boiling in vacuo.

In the table are given the values of the mass susceptibility of mercury obtained with mercury distilled in air at a pressure of 2 cm. and later boiled in an evacuated tube; the absolute value at 20° C. is taken to be 0.1680×10^{-6} c.g.s. units per gram.

χ (c.g.s.u. $\times 10^{-6}$)	T (°C.)	χ (c.g.s.u. $\times 10^{-6}$)	T (°C.)	χ (c.g.s.u. $\times 10^{-6}$)	T (°C.)
0.1681	18.5	0.1653	110.5	0.1639	196.0
0.1668	42.0	0.1648	131.5	0.1639	203.5
0.1666	60.0	0.1644	154.0	0.1637	226.5
0.1656	75.0	0.1642	172.0	0.1640	247.5
0.1654	91.2	0.1641	184.5	0.1637	287.5

The temperature variation of the magnetic susceptibility of metals has been extensively discussed by Stoner⁽⁴⁾ and others. Stoner suggests that the increases in the paramagnetic susceptibilities of the alkali metals observed by Sucksmith⁽⁵⁾ are due to the change in the maximum energy of an electron in an energy band which for the present purpose may be taken as equal to that of a conduction electron at

absolute zero in Fermi-Dirac statistics, brought about by the expansion of the metals. He deduces that the quantity

$$\left[\frac{(\Delta\chi_A)_e}{(\chi_A)_e} \right] \Delta T$$

should be approximately equal to $\frac{2}{3}\alpha_v$, where $(\Delta\chi_A)_e$ is the change in the magnetic susceptibility $(\chi_A)_e$ of the conduction electrons in 1 gram-atom of metal for a temperature-rise ΔT , and α_v is the volume coefficient of expansion of the metal.

If we take 0.276×10^{-6} as a reasonable value⁽⁶⁾ for the diamagnetic susceptibility χ_a of the core of the mercury atom we have that the susceptibility of the electrons in 1 g. of mercury at 20° C. is

$$\{-0.168 - (-0.276)\} \times 10^{-6} = +0.108 \times 10^{-6} \text{ c.g.s. units.}$$

Now, the change in magnetic susceptibility as the temperature rises from 20 to 300° C. is 0.0043×10^{-6} . The calculated value of $\frac{2}{3}\alpha_v$ is therefore 0.000142 as compared with the experimental value of 0.00012 ; the agreement is striking, to say the least. However, the calculated value of $\frac{2}{3}\alpha_v$ is much affected by the value assumed for the magnetic susceptibility of the mercury core. Thus, if we take Shur's⁽⁷⁾ experimental value for the susceptibility of the mercury-vapour atom, viz. $-78 \pm 7 \times 10^{-6}$ c.g.s. units per gram-atom, as representing the diamagnetism of the core, we have

$$(\chi_A)_e = \{-0.168 - (-0.378)\} \times 10^{-6}$$

giving

$$(\Delta\chi_A)_e / (\chi_A)_e \cdot \Delta T = 0.000073,$$

and the agreement with Stoner's theory is not as good. Again, if we take Kido's⁽⁸⁾ experimental value -40.4×10^{-6} c.g.s. units per gram-ion for the Hg^{++} ion, as substantially the same for the mercury core, we get a calculated value for $\frac{2}{3}\alpha_v$ about four times too high.

It seems clear that the magnetic discontinuities described above cannot be attributed to occlusion of gases in the mercury. The quantity of occluded oxygen necessary to produce the observed changes is so considerable that in view of the doubts which have always been expressed with regard to suggestions that mercury occludes measurable quantities of oxygen or nitrogen, it is necessary to submit another reason for the discontinuities. It is suggested that, in the absence of a minute trace of gas, mercury atoms associate to form molecular groups with large electron-orbits such as have recently been postulated by Pauling⁽⁹⁾, by Lonsdale⁽¹⁰⁾, and by London⁽¹¹⁾ to explain the magnetic anisotropy of aromatic compounds, whereas the presence of gas would prevent such association. It is difficult perhaps to reconcile this picture with the fact that mercury distilled at the higher air pressure of 5 cm. was more diamagnetic in experiments (a) than in experiments (b), but it must be remembered that in this case the rate at which the mercury distilled was so great that the purity of the distillate may legitimately be suspect. Bailey, Fordham and Tyson⁽¹²⁾ have proved fairly conclusively that there is always a thin crystalline skin of some adventitious impurity upon the surface of mercury even though special precautions be taken to prevent its formation. It is difficult to see why the impurity

should be confined to the surface of the mercury alone, and we submit that the magnetic measurements prove that it is not. For on the contrary view we must presume the existence of a highly paramagnetic skin over the whole of the mercury in contact with the glass tube used in the magnetic experiments. However, the main purpose of this note is to draw attention to the fact that mercury purified by the Hulett method is more satisfactory for research purposes when it is subsequently heated in vacuo for some time.

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A NEW FORM OF FREQUENCY AND TIME STANDARD

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ABSTRACT. A description is given of a new form of quartz oscillator, designed to give a high frequency-stability under conditions of operation demanding little attention. It consists of a cylindrical quartz ring whose mean radius is about 2·7 cm., oscillating in an overtone longitudinal mode at a frequency of 100 kc./sec. The elastic wave round the circumference has six nodes, and the ring is supported at three of these nodes so as to be located with almost geometric precision with respect to the electrodes, with no constraints acting on it except those due to its own weight. Since the mean circumference of the ring remains unchanged during the vibration there is little air damping, and strong oscillations are obtained at atmospheric pressures. The temperature coefficient of frequency depends on the difference between the internal and external radii of the ring and can be reduced to zero at a particular temperature, the average coefficient being less than 1 part in 10^6 per 1°C . for temperatures 15°C . above and below that value. The frequency-stabilities of two equipments are given. An oscillator at room-temperature and atmospheric pressure, and not maintained in continuous operation, gives a stability of ± 5 parts in 10^9 during periods of an hour, and ± 1 part in 10^7 during weekly periods. An oscillator maintained in continuous operation in an evacuated container at a controlled temperature, and used as a standard of time, gives a stability of ± 4 parts in 10^{10} during hourly periods, and 1 part in 10^8 during monthly periods.

§ 1. INTRODUCTION

THE quartz resonator was first used as a standard of frequency by Professor Cady in 1922, and it was some time after this that the resonator was successfully incorporated in a valve oscillatory circuit to control the frequency of electrical oscillations. Such rapid progress has been made in this field, however, that now the quartz oscillator not only is widely used for stabilizing the frequency of transmitting stations but also constitutes the most accurate means of recording the passage of time. The highest long-period frequency-stability attainable by the ordinary quartz plates used for controlling the frequency of transmitting stations is of the order of several parts in 10^6 , and that attainable by the best quartz frequency and time standards is 1 part in 10^8 . There is still a definite need for an oscillator which gives a stability considerably better than 1 part in 10^6 and is yet reasonably inexpensive, robust, portable, and calls for little maintenance attention.

The main purpose of the work described in the present paper is the development of such an oscillator. Its successful accomplishment, however, automatically provides the basis for a new form of primary standard, for an oscillator that maintains a frequency stability better than 1 part in 10^6 , when operating under

conditions of no particular refinement and with little attention, should give a stability at least as high as any yet attained, when operating under more constant and favourable conditions. An oscillator of the type described has been installed in a manner appropriate for a primary standard and is now in operation as the National Physical Laboratory quartz clock no. 2. A short description of the equipment is included in the paper, together with the results so far obtained.

§ 2. STATEMENT OF THE PROBLEM

It is the author's experience that the frequency-stability of quartz-controlled oscillations depends more on the quartz itself and the manner in which it is supported than on the circuit. It is true that the performance of a poor oscillator may often be improved by modifications of the driving circuit, but if the quartz is suitably mounted so as to have a very low logarithmic decrement, of the order of 10^{-5} , the frequency of oscillation is so little dependent on the circuit conditions that the simplest circuit is quite satisfactory and any risk of trouble arising from unnecessary elaborations is avoided. The investigation was, therefore, confined almost entirely to the quartz and its mounting, and the circuit used differs little from that of the quartz standard already in use at the National Physical Laboratory⁽¹⁾.

As a guide to the development of the new form of quartz oscillator the following particular requirements, regarded as desirable, may be enumerated. (a) The temperature coefficient of frequency should be less than 5 parts in 10^7 per 1°C . so that only a rough form of temperature-control is required. (b) The quartz and the electrodes must be precisely and permanently located with respect to one another. The frequency variation that may be caused by varying the gap between the quartz and the electrodes is of the order of 2 parts in 10^3 , and it is therefore evident that the greatest possible precautions must be taken to prevent any relative displacements. In the first place the quartz should be symmetrically disposed between the electrodes so that the effects due to movement of the quartz tend to compensate, and secondly the quartz and electrodes should be rigidly located. The location should be invariable with temperature, pressure, external vibration and time. (c) The location should be effected in such a manner that the quartz can be easily removed and replaced in exactly the same position. This greatly facilitates the adjustment of the quartz to an exact frequency. (d) It is desirable that the oscillator should be capable of operating at atmospheric pressures, as this also considerably facilitates the frequency-adjustment. (e) It should be possible to adjust the frequency of vibration to within a few parts in 10^6 of the required value by altering the dimensions of the quartz, for if the frequency is suitably independent of external conditions, such as temperature, little adjustment can be made by altering these conditions. A small final adjustment can, however, be effected by the insertion of a suitable capacitance across the quartz electrodes. (f) The variations of frequency with the circuit conditions and the supply voltages should be so small that these do not require any close control. (g) There should be no appreciable drift in frequency after the switching-on of the voltage supplies to the oscillator. It is

clearly inconvenient for many purposes if the oscillator needs to be in continuous operation to give a known, steady value of frequency.

It might be thought that an oscillator similar to the best quartz standards at present in use, but made in a somewhat cheaper, less elaborate form, would fulfil the above conditions, but a consideration of their design shows that this is not the case. The standards that, according to published results, have so far given the best performances, are those installed at the Physikalisch-Technische Reichsanstalt⁽²⁾ and the National Physical Laboratory⁽¹⁾.

Those at the former institute consist of quartz bars about 9 cm. long held at the nodes by silk or wire threads and mounted in evacuated glass tubes. Two types are used, one having a temperature coefficient of about -3 parts in 10^6 per 1°C ., and the other, later, type a few parts in 10^8 per 1°C . at a particular temperature. Although these possess many desirable characteristics it seems that it is very difficult to adjust the frequency to a precise value, for most of the oscillators of this form reported on differ from their nominal value by several parts in 10^5 .

The standard at the National Physical Laboratory consists of a quartz ring of diameter approximately 10 cm., suspended between the electrodes by means of three fine wire stirrups. It operates in an evacuated glass vessel, and its temperature coefficient is about -2.5 parts in 10^6 per 1°C . The large size of this ring, its rather high temperature coefficient, and the fact that its level must be carefully preserved, make it quite unsuitable for standards of the type here considered.

§ 3. THE NEW FORM OF OSCILLATOR

A number of preliminary experiments were carried out with bars and rings of quartz and with different systems of mounting, and the form now described was chosen as most nearly fulfilling the requirements enumerated in the previous section. A very brief description of it was given in a letter published in *Nature*⁽³⁾ in 1935.

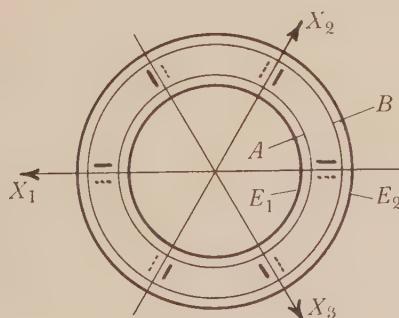


Figure 1.

It consists of a hollow cylindrical quartz ring whose axis is in the direction of the optic axis of the crystal. The two electrodes are coaxial metal rings E_1, E_2 , figure 1, at a distance of about 2 mm. inside and outside the cylindrical surfaces of the quartz. There are three electric axes X_1, X_2, X_3 in the plane of the ring. An

electric field across the electrodes therefore produces, by virtue of the converse piezoelectric effect, circumferential strains which vary in amplitude round the ring and are of opposite sign at points 60° apart. An alternating electric field produces alternating circumferential strains which are of opposite phase at these points. When the frequency of the applied alternating field equals the appropriate natural frequency of the quartz ring, a strong longitudinal, compressional vibration round the circumference of the ring is excited, and considerations of symmetry indicate that the vibration of this kind of lowest frequency is one having nodes at the six sectional areas where the planes containing the electric axes and the cylindrical axis cut the ring. This overtone longitudinal vibration having six nodes and three complete waves round the circumference is the one used in the new form of oscillator. The mean circumference remains constant during the vibration, so that there is no deformation of the ring except periodic changes in the cross-sectional dimensions, which vary in phase and amplitude round the circumference.

The frequency of vibrations of this kind in a ring of small circular cross-section is given by the formula⁽⁴⁾

$$N = \frac{\sqrt{1 + S^2}}{2\pi} \cdot \frac{q}{ap} \text{ c./sec.}$$

in which q is the Young's modulus, ρ the density, a the mean radius, and S the number of waves round the circumference. Inserting the appropriate values for quartz, $q = 7.85 \times 10^{11}$, $\rho = 2.65$ and taking S equal to 3, we have

$$N = \frac{2.735}{a} \times 10^5 \text{ c./sec.}$$

Since the rings actually used are of approximately square section, the sectional dimensions being comparable with the mean radius, the above formula would not be expected to apply exactly. An empirical formula obtained from measurements of a number of rings is

$$N = \frac{2.67}{a} \times 10^5 \text{ c./sec.}$$

The frequency, depending only on the mean radius, can be adjusted in either direction by grinding the inside or outside cylindrical surface as the case may be. The fineness of adjustment is such that it is necessary to grind with an abrasive powder for several minutes to change the frequency by 1 part in 10^5 . The frequency of 100 kc./sec. was chosen as being the most suitable from several different considerations. It gives a ring of convenient size, the mean radius being 2.67 cm. It enables the ready control of multivibrators at frequencies of 1, 10, 100, and 1000 kc./sec., which are almost universally employed in modern methods of frequency measurement, and if the ring is to be used for controlling the frequency of a transmitter, not many stages of frequency-doubling would usually be required to derive the transmitter frequency from a frequency of the order of 100 kc./sec.

§ 4. THE ELECTRODES AND METHOD OF MOUNTING

An assembly drawing of the quartz ring and electrodes is shown in figure 2. The internal electrode 1 is cut from a solid brass rod, so that three arms 2 spaced at 120° are left projecting. The arms carry chisel-ended phosphor-bronze screws 3 whose chisel ends are thinned down to a thickness of about 0.25 mm., rounded, and polished. These polished ends are located in V-shaped grooves, 0.25 mm. deep, cut radially in the lower face of the quartz at three nodal positions. The quartz is thus located with respect to the electrode with almost geometric precision and is yet under no restraints except those arising from its own weight. The outer electrode 4

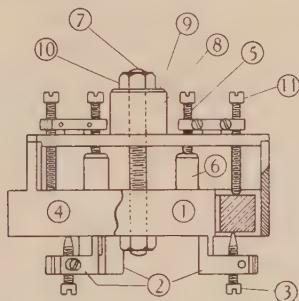


Figure 2.

is located in a similar manner with respect to the inner electrode. Three screws 5 with rounded and polished ends, and carried by a spider fixed to the electrode, fit into V-shaped grooves cut radially in the fused-quartz pillars 6, which are fixed in the inner electrode. The three units of the oscillator are thus very precisely located and can be taken apart and reassembled without the relative positions being changed. In order to make the system completely portable, the two electrodes are held in position by means of the brass bolt 7, fused-quartz insulating tube 8, brass cap 9, and nut 10; and the screws 11, with rounded and polished ends, are screwed down and locked at a distance of 0.01 mm. from the upper surface of the quartz ring, so that though they do not constrain it in any way, they prevent the bottom locating screws from leaving the grooves in the ring.

§ 5. LOCATION OF THE NODAL POINTS

It was expected that the nodes of vibration would approximate to the areas where the planes containing the electric axes X_1, X_2, X_3 , figure 1, and the cylindrical axis cut the ring. The experimental investigation was limited to the determination of the nodal points on the two plane surfaces of the ring. For this purpose the ring was supported between the electrodes on three metal balls spaced symmetrically round its mean circumference, and it was rotated on these in the direction of the circumference until it oscillated with maximum amplitude. The three points of contact were then assumed to be three of the six nodal points. The next position of maximum amplitude determined the other three nodal points. The ring was then turned over and the six nodal points on the other surface were determined.

These positions were easily located with an accuracy of 1° of rotation. They are shown in figure 1 as full lines for the nodes on the top surface of the quartz and broken lines for those on the under surface. It is seen that the nodes on the two surfaces lie in planes inclined at considerable angles to those formed by the electric and cylindrical axes, and that these inclinations are of opposite senses for neighbouring pairs of nodes. The value of the angle of inclination for the four rings whose dimensions are given in table 1 is 35° . This means that for rings of a thickness of 1 cm. in the direction of the optic axis, the nodal points on the front surface, as viewed in figure 1, are displaced by 3.5 mm. in a clockwise direction from the electric axes, and those on the back surface are displaced by the same amount in an anti-clockwise direction.

Table 1

Quartz ring no.	Outer diameter (mm.)	Inner diameter (mm.)	Mean diameter (mm.)	Width (mm.)	Thickness in direction of optic axis (mm.)	Temperature at which temperature coefficient is zero ($^{\circ}\text{C}$)	Frequency (kc./sec.)
3	62.4	43.0	52.7	9.68	11.3	55.0	100.00
	62.35	43.5	52.92	9.42	11.3	50.5	100.00
	62.3	43.6	52.95	9.33	11.3	49.0	100.00
	62.15	44.15	53.15	9.00	11.3	45.0	100.00
	61.4	46.8	54.1	7.3	10.7	23.0	100.00
	61.32	46.8	54.06	7.26	10.7	22.0	100.00
4	61.77	44.95	53.36	8.41	10.0	44.0	100.00
	61.70	45.18	53.45	8.26	10.0	42.0	100.00
	61.68	45.18	53.43	8.24	10.0	40.0	100.00
	61.60	45.18	53.39	8.21	10.0	38.0	100.00
2	62.2	43.36	52.78	9.42	11.05	54.0	100.00
	61.44	45.22	53.33	8.11	11.05	25.0	100.00
5	61.70	44.5	53.10	8.6	10.9	31.0	99.27

The inclination of the nodal plane is probably an effect analogous to that described by Straubel⁽⁵⁾ and may be attributed to the difference between the elastic coefficients measured in different directions of the quartz crystal.

The directions of the electric axes were found by applying a mechanical pressure to the cylindrical surfaces at points such as *A*, *B*, all round the ring, and measuring the potential-difference developed as a result of the piezoelectric effect. Maximum potentials are obtained at the points where the electric axes are radial to the ring, and when the potential is negative on the outer surface the direction of the axis is from the centre towards the circumference.

§ 6. TEMPERATURE COEFFICIENT

The temperature coefficient of frequency of the rings depends on the difference between the internal and external radii and on the temperature. The relationship was investigated experimentally by gradually reducing the width of a ring and determining the {frequency, temperature} curve at a number of different values.

A ring of width 10 mm. was cut, and adjusted to have a frequency of 100 kc./sec. The width was reduced by grinding the two cylindrical surfaces by amounts such as to keep the frequency at 100 kc./sec. Figure 3a shows the variations of frequency with temperature at one particular width, and figure 3b gives the relationship between the width of the ring and the temperature at which the temperature coefficient is zero.

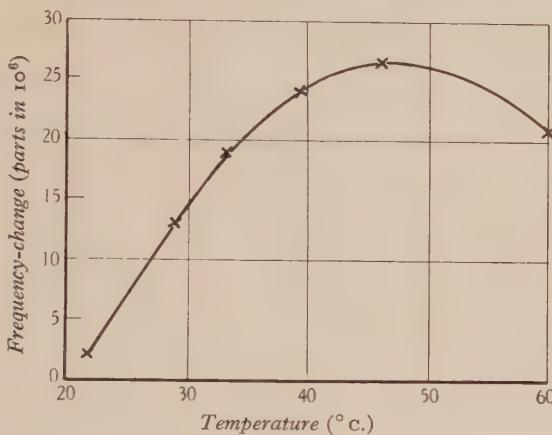


Figure 3a. Variation of frequency with temperature.

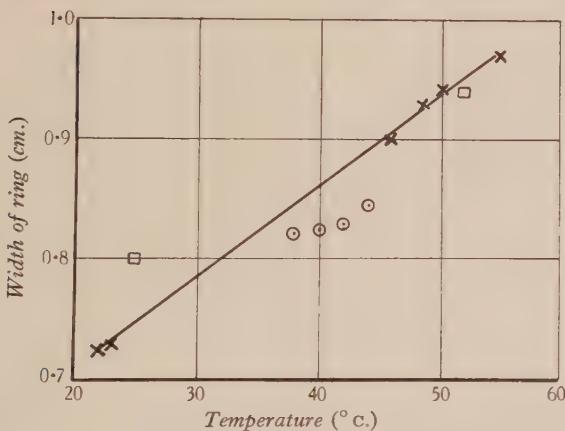


Figure 3b. Variation of maximum of temperature curve with the width of the ring.
 x, ring 3; ○, ring 4; □, ring 2.

When the width was reduced below 9.0 mm., for which value the zero coefficient was obtained at 46° C., the oscillations of the ring became rapidly weaker. It was tested as a resonator and found to resonate feebly at a frequency of about 101 kc./sec., as well as at 100 kc./sec. As the width was further decreased, the resonance at 101 kc./sec. became stronger and the one at 100 kc./sec. weaker, and when the ring finally oscillated again it did so at a frequency of 101 kc./sec. A considerable adjustment was obviously now necessary, and was made by grinding the inside surface only to bring the frequency back to 100 kc./sec. When this was done the width was 7.3 mm. and the zero coefficient was at 23° C. The history and dimensions

of this ring, designated as quartz ring no. 3, are shown in table 1. Another ring, quartz ring no. 4, was tested repeatedly as a resonator, and as soon as the second resonance could be detected, the frequency of this resonance was adjusted to be 100 kc. sec. It then oscillated strongly in this mode when the thickness was 8.41 mm. and the zero coefficient was at 44° C. Quartz ring no. 2 behaved in a similar manner and was satisfactorily adjusted to have a zero coefficient at 25° C. Quartz ring no. 5 behaved somewhat differently, the second mode being only 0.5 kc. sec. removed from the first mode, but it was satisfactorily adjusted to have a zero coefficient at 31° C. Its frequency was adjusted to 99.27105 kc. sec. as the ring was intended to serve as a sidereal time standard at an observatory. A de-multiplication factor of 99,000 gives a frequency of 1.0027379 per mean solar second, or 1.0000000 per sidereal second.

The experience obtained with these four rings shows that 100-kc. sec. oscillators can be made with a zero temperature coefficient at any temperature in the ordinary working range, but that if, as is usually the case, the actual value of the temperature of operation is not important, it is best to adjust the rings to have a zero coefficient in the region 50° C. to 60° C. as no trouble is then experienced with the second resonance. It appears from the close agreement of the dimensions of the different rings that it should be possible to cut a ring to have a frequency within a few parts in a thousand of the required value, with a zero coefficient at a temperature between 50° C. and 60° C.

§ 7. THE ELECTRICAL CIRCUITS

The electrical circuits do not differ in principle from those described by the author in an earlier paper, and it is not thought necessary to give detailed descriptions or diagrams. The Pierce circuit is used for maintaining the quartz in oscillation, and this is followed by a single buffer stage from which the output at 100 kc. sec. is taken. One difference which may be noted is the introduction of a condenser connected across the electrodes of the oscillator. This is a specially designed quartz insulation micrometer condenser which enables the frequency to be changed by a total amount of ± 5 parts in 10^6 , and by 4 parts in 10^9 per scale division. Another new feature is the use of toroidal coils in the driving and buffer circuits. This is found to result in a considerable reduction in the effect of fluctuations of the supply voltages on frequency, possibly owing to the more complete decoupling between the two stages.

For the purpose of measuring the frequency directly in terms of astronomical time signals, an output at the frequency of 100 kc. sec. controls two multivibrators in cascade at frequencies of 10 kc. sec. and 1 kc. sec. respectively. An amplified output at 1 kc. sec. drives a phonic motor from which impulses at 1.0 sec., 0.1 sec. and 0.01 sec. can be obtained, for recording on a chronograph together with the time signals.

§ 8. PERFORMANCE

Frequency variations with changes in circuit conditions. It is obviously desirable to have the fullest information concerning the dependence of frequency on the

circuit conditions, and detailed measurements were made. The results are given in a very condensed form in table 2 to show the degree of stability attained.

Table 2

10 per cent increase of	Frequency-change (parts in 10^8)
Anode voltage	+ 1
Filament voltage	+ 3
Conductance between electrodes	- 4
Value of LC in tuned circuit in anode of driving valve	+ 6
Grid-filament capacitance of driving valve	- 200
Grid-anode capacitance of driving valve	- 200

The effect of coupling an output coil to the anode coil of the driving valve is a change of frequency of about 1 in 10^7 , but there is no measurable change when the output is taken from the buffer valve. The curve showing the variation of frequency with temperature has already been given in figure 3a. Similar curves were obtained for all the rings tested, the only difference being the temperature at which the coefficient was zero. The total change of frequency as the pressure is reduced from 760 mm. to 0 mm. of mercury is of the order of 4 parts in 10^6 , but the pressure coefficient in the region of atmospheric pressure is only about 0.02 part in 10^6 for a change of pressure of 100 mm. of mercury.

The logarithmic decrement of the oscillator is 6×10^{-5} in air and 3×10^{-5} in vacuo. If the oscillator is shaken, or knocked with sufficient violence to make the quartz jump on its supports, frequency changes of as much as one or two parts in 10^7 sometimes occur, but ordinary vibrations of the room such as might be caused by motor generators have no measurable effect. A light spring pressure applied at three of the nodes on the upper surface of the quartz causes the frequency to be completely unaffected by knocking or shaking, but the pressure itself causes a frequency change of a few parts in 10^5 . It is obvious that changes of this pressure could produce quite appreciable variations of frequency, and in the author's opinion the unclamped type is more satisfactory for most purposes. The oscillators whose performances are discussed here are of this type.

Frequency-stability. In view of the twofold object of this work—the production of a simple, robust, standard of frequency, and the incorporation of this in a primary frequency and time standard—the frequency-stability of the oscillator with respect to lapse of time will be considered when it is operating under two different sets of conditions. In the first case an oscillator whose zero temperature coefficient was in the neighbourhood of room-temperature (quartz ring no. 3, table 1) was mounted in a metal pot, which was filled with dry air and then sealed with a rubber gasket. This precaution was to protect the crystal from changes of humidity rather than of pressure. The oscillations were maintained by the simple Pierce circuit, and the voltage supplies obtained from general utility batteries, which were subject to variations in voltage of ± 10 per cent. The oscillator stood on a pad of felt on an ordinary laboratory table in a room where the temper-

variations amounted to $\pm 1^\circ$ C. The temperature of the oscillator was not controlled but followed the variations of the ambient temperature of the room. The frequency was measured at intervals during a period of several months, the voltage supplies to the oscillator being switched on a few minutes before the measurements were made. It was found that the drift after switching on was no more than 1 part in 10^8 , that the frequency-variations during an hour were of the order of $\pm 0.5 \times 10^{-8}$, and that the stability over a period of a week was of the order of $\pm 10 \times 10^{-8}$. There was, however, a slow drift in frequency of about +10 parts in 10^8 per week, which so far has not been explained. This is not regarded as a very serious drawback in a substandard of frequency, since it can be checked periodically by comparison with standard frequency emissions and any necessary adjustment can be made. The important characteristic is the high degree of stability attained when the crystal is operating under conditions demanding little attention.

The other stability-measurements relate to an oscillator installed as a primary standard. Quartz ring no. 2, table 1, was sealed in an evacuated fused-quartz container and housed in an oven controlled to within $\pm 0.01^\circ$ C. at the temperature at which its temperature coefficient is a minimum. The driving, demultiplying, and amplifying circuits were operated by trickle-charged batteries, and the equipment was maintained in continuous operation as quartz clock no. 2. Outputs at frequencies of 100 kc./sec. and 1 kc./sec. were available for purposes of frequency-measurement, and 1-second contacts on the phonic motor were used for comparing the rate of the standard with other time standards and with astronomical signals.

The short-period stability of frequency was determined by combining the 100-kc./sec. outputs of two similar, but entirely independent, oscillators and measuring the period of the beat obtained. Continuous measurements were made for one hour, each measurement being of about 200 seconds' duration. No departures of more than 4 parts in 10^{10} from the mean value of their frequency-difference were observed.

The mean daily rate of the clock was measured by recording the seconds impulses from the phonic motor and the time signals from Paris, Rugby and Hamburg, on a chronograph. The rate averaged over 10 days and for the three sets

Table 3

Date, 1937	Mean daily rate (sec./day) obtained from corrected time signals			
	Paris	Rugby	Hamburg	Mean
March 3 to 13	-0.020	-0.021	-0.019	-0.020
March 13 to 19	-0.021	-0.018	-0.022	-0.020
April 8 to 18	-0.020	-0.020	-0.016	-0.019
April 18 to 28	-0.019	-0.020	-0.023	-0.021
April 28 to May 8	-0.020	-0.021	-0.019	-0.020
May 8 to 13	-0.017	-0.020	-0.021	-0.019
May 16 to 26	-0.016	-0.017	-0.018	-0.017
May 26 to June 5	-0.018	-0.014	-0.017	-0.016
June 5 to 15	-0.015	-0.018	-0.015	-0.016
June 15 to 25	-0.014	-0.019	-0.018	-0.017

of time signals was usually accurate to ± 0.001 sec. per day, when the corrections to the signals had been applied. Although the oscillator has been in continuous operation since March, 1937, it has not been possible to obtain a complete record of its rate, owing to a modification to some of the associated equipment, but the results obtained in table 3 indicate that the performance is as good as that of any clock so far installed.

Although there is again a gradual increase in the frequency of the standard, this is now so small and uniform, that accurate allowance can be made for it when the present rate of the clock is calculated. The latter can be predetermined with a precision of ± 0.001 sec./day, or 1 part in 10^8 .

§ 9. ACKNOWLEDGEMENTS

In conclusion the author wishes to express his appreciation of helpful discussion with his colleagues, in particular Dr L. Hartshorn and Dr G. A. Tomlinson; and also of the interest with which the work has been followed by the superintendent of the Electricity Department, Dr E. H. Rayner.

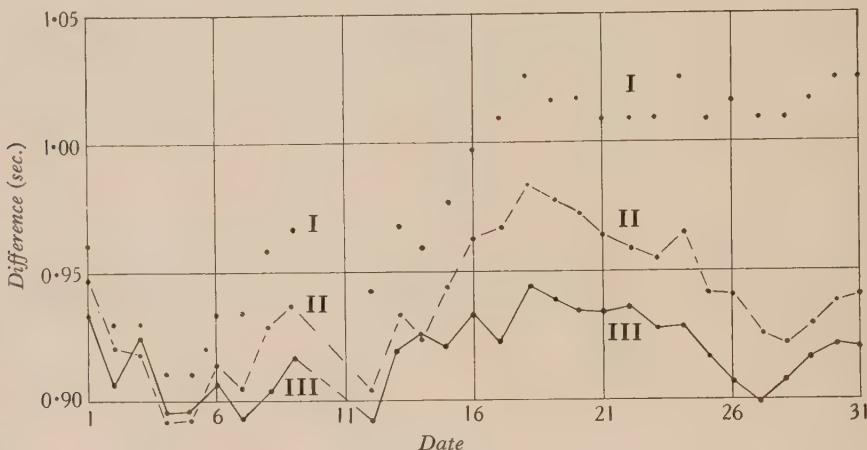
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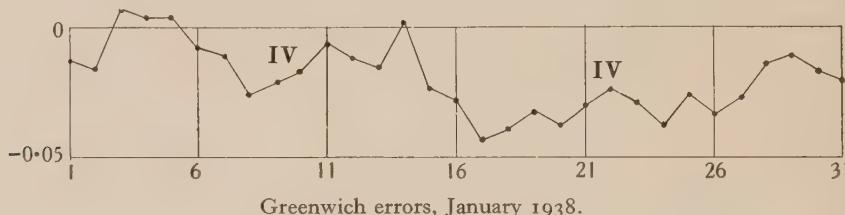
DISCUSSION

Mr E. C. ATKINSON. When the quartz crystal was first used as a clock, the frequency was by no means independent of the working conditions—valve, voltage, temperature and pressure. The author has shown how these interferences have been reduced, notably by arranging to work at a temperature for which the rate is a maximum. He has made an engineer's job of the construction. I am interested in the crystal mainly as a primary standard, and I am looking forward to the time when it will assist in the time service at Greenwich. My clocks are compared with the Greenwich signals and, in the middle of February, I sent a chart to the observatory showing the comparison of my E_{15} with the 10.0-h. rhythmic signal from Rugby for the previous 50 days, before the corrections to this signal for January had been published. These corrections are arrived at after balancing possible irregularities in clock-rates against possible errors in transit determinations of time. The crystal clock will not reduce errors in star observations, but it may assist in estimating their values, for with a perfect clock they would be exactly known. Curve II, corrected for stratification, shows that E_{15} was fast on the Rugby signal between 0.89 sec. and 0.98 sec., a range of 0.09 sec. during January. The Greenwich errors, IV, account for part of this, reducing the range to 0.05 sec. The corrected curve III, except for

the last few days of the month, is similar in general shape to a reflection of the Greenwich chart. A single clock cannot give reliable information about Greenwich errors, but the reflection appearance can be explained on the assumption that the errors are in general greater than those found from the Observatory data, with a range about half as large again.



Extent to which E_{15} is fast on Rugby 10.0-h. rhythmic signal. I, as observed; II, reduced to 2.3°F . stratification, range 0.092 sec.; III, corrected for Greenwich errors, range 0.052 sec.



Greenwich errors, January 1938.

Dr D. OWEN. It is astonishing to learn of the construction of a clock based on the action of a quartz ring oscillating with a frequency of 100,000 c./sec., and to have evidence that it maintains its uniformity within a margin as small as four parts in 10,000 millions, at least for short periods of about an hour. Such constancy appears amply to exceed anything claimed for the Shortt pendulum clock, and this latest type of quartz time-keeper appears to have the further advantage of being independent of gravity. The problem of the degree of uniformity of the earth's rotation would seem to be now within range of definite solution.

Mr D. A. BELL. I believe the advantages of the circular quartz oscillator arise from the absence of faces having large displacements normal to the surface, and the existence of well defined nodes; these features minimize air damping and the effect of supports on the frequency of the oscillator. The shape in question has also the advantage that frequency is little affected by small displacements of the electrodes. The temperature coefficient of frequency of the quartz ring alone can therefore be

made zero, without the need for any allowance for the effect of temperature on the electrode system. The obvious disadvantage, however, is the need for such large volumes of quartz, which must be free from both optical and electrical twinning.

With regard to the very high stability of frequency observed, the figure of 4 parts in 10^{10} for one hour corresponds to a change in phase-difference between two 100-kc./sec. oscillators of about 0.01 cycle at the end of the hour. If the two oscillators compared are of identical quartz-ring construction, is there not a risk of undetected drift of both in the same direction, due to a specific property of this type of oscillator, such as internal heating?

I should be interested to know the sign of the change of frequency with damping, for I wonder whether the extremely small but persistent change given in table 3 (about 3 parts in 10^8 after 4 months) may not be due to a slight change in damping at any part of the system.

Has the thickness of the ring in the direction of the optic axis any influence on the ratio of outer to inner diameter for a given thermal performance? I notice that ring no. 3, 11.3 mm. thick, gave a zero temperature coefficient at 45° C. with a ratio of about 1.41, but ring no. 4, only 10 mm. thick, for 44° C. had a ratio of about 1.37. On the other hand, ring 2 and ring 3, nearly equal in thickness, have ratios of about 1.44 and 1.45 for 54° C. and 55° C. respectively. I should also like to ask whether the thickness has any effect on the second resonance, since the presence of this undesired frequency would be one of the chief difficulties in the manufacture of such oscillators.

Dr F. J. W. WHIPPLE. The author points out that Hoppe's formula for the frequency of vibration of a ring* is not quite consistent with observation; the discrepancy is about 2 per cent. It is worth noticing that Hoppe's formula allows for the radial component in the oscillation, though this component would probably be of less importance in a substantial ring than in the thin one for which the formula is proved. If the radial component were ignored entirely, S would have to be substituted for $\sqrt{(1+S^2)}$ in the formula. Since $\sqrt{10}:3$ is equal to $100:95$, this would imply a reduction of 5 per cent in the calculated frequency; the observed reduction of 2 per cent might well have been anticipated.

AUTHOR'S REPLY. The main purpose of the quartz clocks is, as Mr Atkinson remarks, to smooth out the errors of time-determination during intervals in which no stellar observations are possible. Whether they are more stable over long periods than pendulum clocks is still to be determined, but their present advantages are that they do not appear to be subject to sudden changes of rate, and that a number of such clocks can be intercompared with great accuracy. The time given by a group of three such clocks would be expected to have a very high day-to-day uniformity, and stellar observations need only be used to correct for any gradual departure from the true sidereal time.

It does seem possible, as Dr Owen suggests, that such a group of clocks might be able to reveal changes in the period of the earth's rotation.

* The proof is given in Love's *Treatise on Elasticity*, 2, 183 (1893).

Mr Bell points out that two such clocks might drift in the same direction without the fact being discovered by their intercomparison. This is of course possible, but it is unlikely to happen when the two equipments are completely separate. The probability is still less if the standards are of different types, and I have in fact made check measurements using the present standard, the Dye quartz oscillator, and a quartz bar. The effect of damping on frequency depends, I think, on the nature of the damping. A general loading, such as that due to air or moisture, would probably cause a decrease in frequency, but it is known that an applied mechanical pressure causes an increase in frequency. I think it is very difficult to attribute to any specific cause the small change in frequency that has so far occurred. A few experiments were made to find whether the thickness of the ring affected its performance, and from these it was concluded that between the values of 11.5 mm. and 7 mm. it has little effect as regards either the conditions for zero temperature coefficient or the second mode of oscillation.

Dr Whipple's suggestion appears to be a useful one, but I should not like to comment on it without looking further into the derivation of Hoppe's formula.

A ROTATIONAL ANALYSIS OF BANDS OF LEAD SULPHIDE

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AND

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ABSTRACT. A rotational analysis has been made of the (6, 0), (7, 0), (9, 0), (2, 1), (3, 1) and (4, 1) bands of the A \leftarrow X system of lead sulphide as observed in absorption. The structure of the bands is that which would be given by a ${}^1\Sigma \leftarrow {}^1\Sigma$ transition. A least-squares fit of the B' values obtained gives $B'_v = 0.08560 - 29.55 \times 10^{-5} (v' + \frac{1}{2}) \text{ cm}^{-1}$ whilst $B''_0 = 0.105614 \text{ cm}^{-1}$ and $B'_1 = 0.104741 \text{ cm}^{-1}$. Other constants determined were $D''_0 = -2.573 \times 10^{-8} \text{ cm}^{-1}$, $D'_0 = -2.508 \times 10^{-8} \text{ cm}^{-1}$, $r_e'' = 0.7552 \text{ Å}$ and $r_e' = 0.8406 \text{ Å}$. The bands analysed were due to ${}^{208}\text{PbS}$, whilst a considerable number of lines observed were accounted for as due to ${}^{206}\text{PbS}$ and ${}^{207}\text{PbS}$.

§ 1. INTRODUCTION

THE band spectrum of lead sulphide was first observed by Rochester and Howell⁽¹⁾. The absorption spectrum of this molecule, as observed by them, stretched from $\lambda 3100$ to $\lambda 8500$ and consisted of overlapping progressions of bands degraded to the red. Five systems were recognized; these had a common ground state and were represented by the following equations:

$$\begin{aligned} \text{System A: } & v = 18,851.3 + 261.09 (v' + \frac{1}{2}) - 0.365 (v' + \frac{1}{2})^2 \\ \text{, , B: } & v = 21,847.7 + 282.17 (v' + \frac{1}{2}) - 0.856 (v' + \frac{1}{2})^2 \\ \text{, , C: } & v = 23,212.9 + 303.93 (v' + \frac{1}{2}) - 1.436 (v' + \frac{1}{2})^2 \\ \text{, , D: } & v = 25,024.4 + 283.95 (v' + \frac{1}{2}) - 1.171 (v' + \frac{1}{2})^2 \\ \text{, , E: } & v = 29,650.5 + 299.34 (v' + \frac{1}{2}) - 1.574 (v' + \frac{1}{2})^2 \end{aligned}$$

$$\begin{aligned} & - 428.14 (v'' + \frac{1}{2}) \\ & + 1.201 (v'' + \frac{1}{2})^2. \end{aligned}$$

In passing, it is of interest to note that there is a quite definite parallelism between the structure of the spectrum of lead sulphide and that of plumbic oxide.

§ 2. EXPERIMENTAL DETAILS

The lead sulphide vapour was obtained by heating lead sulphide in a vitreosil or alundum tube surrounded by a wider iron tube, the composite tube being placed in an electric furnace having Silit rod heating elements. The internal diameter of the inner tube was 3.8 cm. and the furnace length was 30 cm. The temperature employed ranged from 800° to 1000° C. Actually, of course, only the middle portion of the tube (probably some 8 cm.) was at the temperatures quoted. The composite

tube was employed for the sole reason that the absorption tubes had to be as thick-walled as possible because of the destructive action of lead sulphide on all the materials available, vitreosil, alundum, and glazed and unglazed porcelain. However, the outer metal tube also was of use in that its higher conductivity would help to lengthen the heated column.

The spectrograms were obtained in all orders from the first to the fourth of the 21-ft. Rowland grating in the University of Manchester Physics Department. This grating is now in a Paschen mounting⁽²⁾ which is extremely suitable for the type of work under consideration, in that a number of spectrograms can be obtained simultaneously, in different orders if necessary. The iron arc was used throughout as a comparison spectrum.

§ 3. ANALYSIS

Owing partly to the complexity of the spectrum and partly to the temperature found necessary to give reasonable absorption it has only been possible to analyse six bands out of the 230 listed by Rochester and Howell. The bands analysed belong to the A system (i.e. $A \leftarrow X$), and table 1 gives the data for them. It will be seen that three of the bands, namely (6, 0), (8, 0) and (9, 0), arise in the ground state ($X, v'' = 0$) and the other three, namely (2, 1), (3, 1) and (4, 1), in the first excited level of this ground state. The group with v'' equal to 0 were photographed in the fourth order of the grating and the others in the second order. These bands were fairly easily resolved into P and R branches, with the exception of (4, 1), in which the two branches coincide. No evidence for a Q branch was found, but since, as the analysis shows, the origin is close to the head (where the lines could not be separated) it is not impossible that a short Q branch exists. However, on the evidence available it seems probable that the spectrum is due to a ${}^1\Sigma \leftarrow {}^1\Sigma$ transition.

Analysis depends on the theoretical formula

$$R(J-1) - P(J+1) = 4B''(J + \frac{1}{2}) + 8D''(J + \frac{1}{2})^3 \quad \dots\dots(1),$$

where

$$D'' = -4B''^3/\omega^2 \quad \dots\dots(2),$$

the symbols having their usual significance.

The bands (8, 0) and (9, 0) were measured first, and it was found impossible to decide which was the better of two arrangements of ($R - P$) differences, for each gave nearly identical values in both bands. However, on measurement of (6, 0) it was at once possible to decide between the alternatives.

Although the above procedure gave us lines having corresponding values of J it did not determine the absolute values of the J s, and this proved to be the main difficulty of the analysis. On rewriting equation (1) in the form

$$\{R(J-1) - P(J+1)\}/(J + \frac{1}{2}) = 4B'' + 8D''(J + \frac{1}{2})^2 \quad \dots\dots(3),$$

and evaluating the left-hand side for trial sequences in J , it was readily found that the values of J were near those given in table 1 and that B'' had approximately the value 0.105 , so that, from equation (2), $8D''$ is approximately -2×10^{-7} . The ω in equation (2) was obtained from the vibrational analysis of Rochester and

Table 1. Lead sulphide bands

J	(6, o) band				(8, o) band				(9, o) band			
	P branch		R branch		P branch		R branch		P branch		R branch	
	v	Int.	v	Int.	v	Int.	v	Int.	v	Int.	v	Int.
27												
28												
29	20,294·09	3										
30	92·55	2										
31	91·05	2										
32	89·46	2										
33	87·83	2										
34	86·20	2										
35	84·62	2										
36	82·71	2										
37	80·97	2d	20,293·58	2								
38	79·09	2	92·06	2								
39	77·20	2	90·63	2								
40	75·28	3d	89·01	2								
41	73·53	3d	87·38	2								
42	71·44	3d	85·73	2								
43	69·37	3	83·95	2								
44	67·32	4	82·20	2								
45	65·21	5d	80·41	2								
46	63·08	5	78·62	2	20,772·63	3						
47	60·76	4	76·70	2	70·44	2						
48	58·46	5	74·80	2	68·05	3d						
49	56·15	5	72·77	3	65·55	3b						
50	53·87	4	70·77	3	63·40	2d						
51	51·39	4	68·69	3	60·93	2-						
52	48·96	5	66·61	3	58·39	2						
53	46·52	6	64·54	4	55·81	1	20,773·62	2				
54	43·97	5	62·07	3	53·36	2d	71·35	3				
55	41·45	5	60·01	3	50·54	2-	68·98	3+				
56	38·78	5	57·80	5	47·90	3	66·75	3d				
57	36·10	5	55·38	3	45·17	2	64·49	4b	20,998·52	2		
58	33·44	5	53·08	4	42·32	3+	61·81	2d	95·66	1	17·54	2-
59	30·64	6	50·63	4	39·59	2	59·36	2	99·30	4	15·03	2
60	27·85	5	48·16	4	36·61	3	56·80	2	92·66	2d	12·53	5
61	25·03	6	45·64	5	33·78	3-	54·23	3	89·89	2	09·99	3
62	22·07	6	43·15	5	30·76	3+	51·61	3	87·02	2	07·38	3
63	19·26	6	40·52	3	27·80	3-	48·93	3	83·95	1	04·63	1
64	16·22	6	37·90	5	24·69	2	46·24	2d	77·84	1	20,999·15	3
65	13·18	5d	35·21	4	21·71	3	43·44	3+	74·75	3	96·40	3
66	10·19	5	32·51	5	18·50	2	40·64	3	71·54	1	93·52	3d
67	07·17	5	29·77	5	15·30	2	37·73	3	68·31	1	90·55	3
68	04·02	5	26·92	5	12·13	2	34·79	3d	65·03	2	87·64	2
69	200·77	4	24·10	5	08·83	2	31·84	3+	61·68	2	84·61	5
70	197·68	5	21·19	6	05·50	3	28·88	3	58·30	1	81·57	3
71	94·32	5	18·20	5	702·13	3	25·84	3	54·90	3	78·52	3
72	91·02	5	15·24	6	698·73	3	22·73	3	51·44	3	75·36	3
73	87·60	4	12·15	5	95·30	3	19·57	3	47·92	2	72·12	3
74	84·27	5d	09·14	5d	91·76	3	16·42	3	44·35	1	68·98	3
75	80·89	5d	06·01	5	88·21	2+	13·25	3	40·71	1	65·60	2
76	77·35	5	202·86	5	84·63	2	09·93	3	37·13	2-	62·33	2
77	73·93	5	199·63	4	80·98	3	06·58	3	33·43	2	59·05	3
78	70·21	5	96·36	5	77·28	3-	703·23	3	29·66	3-	55·50	2
79	66·65	5	92·99	5	73·58	3	699·82	3+	25·94	1	52·01	2
80	63·02	5b	89·67	5	69·80	3-	96·40	3+	22·07	2-	48·53	2
81	59·22	5	86·38	5d	65·98	3	92·95	3	18·13	2	45·01	2
82	55·48	5	82·99	5d	62·11	2+	89·40	3d	14·28	2-	41·38	2
83	51·61	5	79·36	4	58·17	3	85·76	3	10·31	1	37·77	2
84	47·78	4	75·94	5	54·25	3	82·07	3+	06·36	2	33·99	3
85	43·89	5	72·53	5	50·22	3	78·41	3	02·23	1+	30·31	3
86	39·87	4	68·78	5	46·13	3	74·64	3+	20,898·11	2	26·49	2+
87	35·95	5	65·18	5b	42·14	3+	70·90	3d	93·99	3	22·69	3
88	31·96	5d	61·48	5	37·91	3	67·08	3	89·77	2	18·83	3
89	27·80	5	57·62	5	33·78	3	63·21	3	85·54	2-	14·92	2+
90	23·83	4	53·92	5	29·52	3	59·33	3	—		10·99	2+
91	19·54	4	49·96	5	25·25	3	55·32	3	76·97	2	06·90	2+
92	15·38	5	46·16	4	20·96	3	51·36	3	72·55	2-	02·79	2+
93	11·20	5b	42·17	5d	16·59	2-	47·20	3			898·66	2+
94	06·78	4	38·19	6	12·17	3-	43·18	3+			94·54	3
95	102·47	5d	34·30	5	07·86	2d	39·93	3			90·36	2
96	98·11	6b	30·36	6d	603·28	3	34·81	3+			86·08	2
97	93·82	5b	26·09	4			30·61	3			81·72	2+
98	89·23	5d	21·87	5			26·35	3			77·50	2-
99	84·62	7d	17·75	5			22·01	3			72·99	2
100	80·18	5d	13·44	5			17·64	2-				
101	75·65	5b	09·16	4b			13·30	3				
102	70·98	5b	04·81	4			08·75	3				
103	66·33	5d	100·39	5b			04·35	3+				
104			95·95	4d								
105			91·52	6								
106			87·01	5b								
107			82·43	5d								
108			77·87	5b								
109			73·37	5b								
110			68·74	5b								
111												
112												
113												
114												
115												
116												
117												
118												
119												
120												

Notes to Table 1. In every case in which there is a gap in the above table a line was actually observable but was so smeared that b means "broad".

A system

(2, 1) band				(3, 1) band				(4, 1) band			
P branch		R branch		P branch		R branch		R branch			
ν	Int.	ν	Int.	ν	Int.	ν	Int.	ν	Int.	ν	Int.
18,842·43	I										
41·19	I										
39·69	2										
—											
37·17	I			19,097·01	I						
35·60	I			95·67	I						
34·11	I			94·29	2						
32·68	I			92·58	I						
31·12	I	18,843·13	I	—							
—		41·85	I	89·50	I						
27·94	I	40·56	I	87·93	I						
26·22	I	—		86·31	2						
—		38·11	1d	84·50	I	19,097·65	I				
22·71	I	36·40	I	82·85	I	96·22	I				
20·95	I	34·93	2b	81·12	I	94·82	I				
19·06	I	33·47	I	79·31	2	93·30	I				
17·22	I	31·88	I	77·48	2	91·81	1d				
15·43	I	—		75·54	2	90·20	I				
13·42	I	28·67	I	73·61	3	88·68	I				
11·33	I	27·02	I	71·65	2	86·94	2				
09·48	1d	—		69·69	2	85·27	I				
07·26	I	23·62	I	67·52	2	83·57	I				
05·02	I	21·84	I	65·38	2	81·77	I				
02·97	I	20·05	2	63·34	3	80·07	I				
00·74	2	18·17	I	61·15	3	78·10	2				
18,798·50	I	16·24	I	58·88	3	76·20	2				
96·26	2	14·62	2b	56·58	3	74·29	3				
94·20	3	12·35	I	54·32	3	72·30	2				
91·53	2	10·38	I	52·03	3	70·34	2				
89·01	3	8·18	2	49·56	3	68·12	2				
86·68	2	6·19	I	47·08	3	66·15	2				
84·15	2	4·01	2	44·79	3	63·93	3				
81·62	2	0·81	2	42·21	4	61·86	2				
79·12	2	18,799·55	3	39·59	3	59·59	3				
76·59	2	97·33	2	36·94	3	57·35	3				
73·89	2	95·03	I	34·43	3	55·03	3				
71·12	3	92·66	I	31·64	2d	52·80	3				
68·43	2	90·19	3	28·96	4	50·36	3				
65·79	2	87·86	2	26·09	4	47·96	3				
63·08	2b	85·32	3	23·42	4	45·45	3				
60·13	2	82·79	I	20·53	4	42·96	4				
57·04	2	80·31	2	17·69	3	40·64	3				
54·12	2	77·76	2	14·79	3	37·74	3				
51·22	3	74·89	2	11·71	3	35·24	3				
48·21	2	72·67	2b	08·79	2d	32·38	4				
45·19	2	69·72	I	19,002·61	2d	29·73	4				
42·06	2	67·19	2b	18,999·46	I	26·95	4				
38·81	3	63·98	3	96·28	2	24·34	3d				
35·73	2	61·21	3	93·12	2	21·39	4				
32·43	2	58·41	I	89·88	2	18·48	3				
29·23	3	55·40	2	86·43	2	15·66	3				
25·86	3	52·46	I	83·05	2	12·54	3				
22·41	3	49·43	2	79·79	I	09·55	2d				
19·22	1d	46·42	2	76·30	2	06·47	2				
15·75	2d	43·36	1d	72·81	2	03·43	2				
12·32	2	39·93	2d	69·07	2	19,000·38	2				
08·70	2	36·93	I	65·77	2	18,997·08	2				
04·96	2d	33·70	3	62·21	2	93·83	2				
30·38	2d	58·48	2	59·53	2	90·53	2				
27·03	2	54·81	2	87·31	2	93·70	2				
23·83	I	51·08	2	83·91	2	36·28	4				
20·57	1d	47·32	2	80·45	2	32·74	4				
17·01	2d	43·58	2	77·09	2	29·33	4				
13·56	2	39·68	2	73·52	2	25·70	4				
10·13	2	35·76	2	70·06	2	22·09	4				
06·37	I	31·85	2	66·47	2	18·48	4				
		27·91	2	62·99	2	14·74	4				
		23·90	2	59·28	2	11·01	4				
		19·90	2	55·69	2	07·32	4				
		15·83	2	51·78	2	03·55	4				
		11·49	2	48·12	2	199·68	4				
		07·42	2	44·25	2	95·72	4				
		90·320	2	40·40	2	91·70	4				
		898·91	2	36·47	2	87·73	4				
		94·63	2	32·50	2	83·80	4				
		90·29	2	28·58	2	79·62	4				
		85·95	2	24·47	2	75·54	4				
				20·46	2	71·38	4				
				16·40	2	67·19	4				
				12·16	2	63·02	4				
				07·96	2	58·64	4				
				903·79	2	54·24	4				
				899·57	2	49·98	5				
				95·18	2	45·53	4				
				90·80	2	41·12	4				
				86·31	2	36·50	4				
						31·93	4				
						27·28	4				
						22·75	4				
						18·09	4				
						13·34	4				
						08·64	3d				
						03·75	3b				
						098·83	4				
						94·29	2				

out by superposition of other lines that no measurement was possible. The symbol *d* means "diffuse"

Howell. The smallness of D'' shows that the right-hand side of equation (3) must be very nearly constant, and we could limit the values of J as being either those given in table 1, or greater than them by unity. This difficulty, of course, arises from the fact that the values of J are all large, so that the quotient in equation (3) is never critical.

We could hope to derive help in this dilemma by calculating the upper-state constants B' and D' from the formula

$$\{R(J) - P(J)\}/(J + \frac{1}{2}) = 4B' + 8D'(J + \frac{1}{2})^2 \quad \dots\dots(4),$$

where D' is given by the analogue of equation (2) and ω is again obtained from the original work. However, we met with exactly the same difficulty, both sets of values of J giving nearly equally constant results. The difficulty was only removed

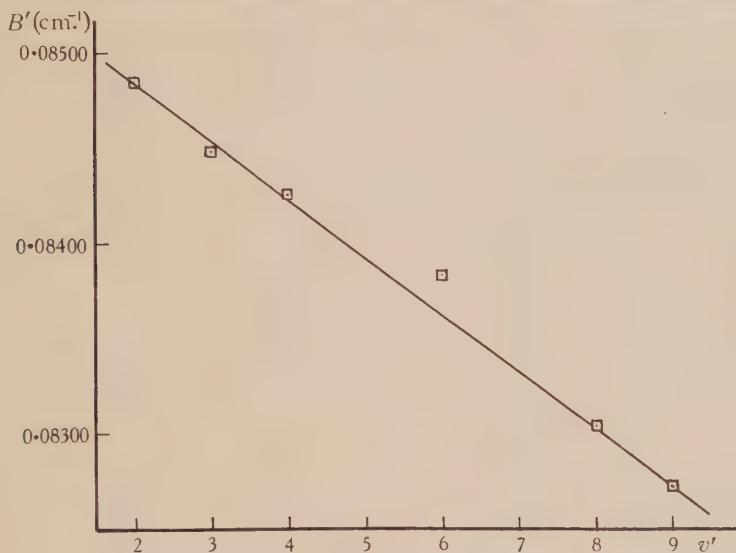


Figure 1. Variation of B' with v' .

with the aid of the bands (2, 1), (3, 1) and (4, 1). The values of J for these bands could in turn not be decided absolutely, but we had the additional checks that the B_1'' derived from them must be smaller than B_0'' and that the values of B' , that is to say of B_2' , B_3' and B_4' , must be nearly linear with the values of B_6' , B_8' and B_9' derived earlier. That the latter condition is fulfilled by our ultimate choice is shown in figure 1.

Having determined uniquely the proper values of J for each branch of each band, we can proceed in the usual way to determine the constants B and D . The rotational term differences were extracted, those for the lower states being given in table 2. Using an approximate value for D_0'' in equation (3), we obtain a value of B_0'' for each difference, every difference being given equal weight so that a simple mean was taken. Using this nearly correct value of B_0'' we recalculate D_0'' from equation (2), using this improved value in equation (3), and recalculate B_0'' . We continue this process until constant values are obtained.

Table 2. Rotational term differences for the ground state

$$R(J-1) - P(J+1) = F''(J+1) - F''(J-1)$$

J	$v''=0$			$v''=1$		
	$v'=6$	$v'=8$	$v'=9$	$v'=2$	$v'=3$	$v'=4$
36				15.19		14.97
37				15.63		15.79
38	16.38					16.32
39	16.78				16.53	16.58
40	17.10			17.16	16.91	16.88
41	17.57			17.34	17.34	17.52
42	18.01			17.71	17.76	17.75
43	18.41			18.04	18.20	17.50
44	18.74			18.46	18.55	18.34
45	19.12				18.99	18.80
46	19.65			19.19	19.42	19.85
47	20.16			19.76	19.89	19.56
48	20.55				20.23	19.94
49	20.93			20.65	20.62	20.44
50	21.38			21.10	21.19	21.23
51	21.81		21.64	21.55	21.52	21.20
52	22.17		22.22	21.91	21.88	21.91
53	22.64		22.68	22.04	22.26	22.78
54	23.09	23.08	22.88	23.09	22.74	23.11
55	23.29	23.45	23.33	23.34	23.26	23.80
56	23.91	23.81	23.89	23.70	23.33	23.29
57	24.36	24.43	24.36	24.03	23.94	24.27
58	24.74	24.90	24.88	24.57	24.34	24.49
59	25.23	25.20	25.14	24.89	24.92	24.72
60	25.60	25.58	25.51	25.22	25.16	25.20
61	26.09	26.04	26.04	25.66	25.71	25.98
62	26.38	26.43	26.43	26.21	26.07	26.15
63	26.93	26.92	26.79	26.60	26.71	26.53
64	27.34	27.22	27.13	26.87	26.94	26.79
65	27.71	27.74	27.61	27.11	27.43	27.17
66	28.04	28.14	28.09	27.73	27.76	27.79
67	28.49	28.51	28.49	28.28	28.17	28.21
68	29.00	28.90	28.87	28.67	28.93	28.62
69	29.24	29.29	29.34	29.09	28.95	28.97
70	29.78	29.71	29.71	29.55	29.60	29.63
71	30.17	30.15	30.13	29.70	29.77	29.94
72	30.60	30.54	30.60	30.61	30.27	30.24
73	30.97	30.97	31.01	30.91	30.67	30.72
74	31.26	31.36	31.41	31.46	31.22	31.21
75	31.79	31.79	31.85	31.55	31.51	31.55
76	32.08	32.27	32.17	31.98	32.05	32.08
77	32.65	32.65	32.67	32.55	32.61	32.39
78	32.98	33.00	33.11	32.99	32.75	32.88
79	33.34	33.43	33.43	33.24	33.25	33.30
80	33.77	33.84	33.88	33.68	33.66	33.62
81	34.19	34.29	34.25	34.10	34.36	34.02
82	34.77	34.78	34.70	34.66	34.61	34.54
83	35.21	35.15	35.02	34.97	34.87	34.91
84	35.47	35.54	35.54		35.35	35.43
85	36.07	35.94	35.88		35.72	35.84
86	36.58	36.27	36.32		36.23	36.15
87	36.82	36.73	36.72		36.59	36.60
88	37.38	37.12	37.15		36.87	37.02
89	37.65	37.56			37.41	37.63
90	38.08	37.96	37.95		37.76	37.97
91	38.54	38.37	38.44		38.21	38.29
92	38.76	38.73			38.56	38.86
93	39.38	39.19			39.09	39.20
94	39.70	39.34			39.38	39.63
95	40.08	39.90			39.86	40.13
96	40.48				40.29	40.53
97	41.13				40.70	41.04
98	41.47				41.05	41.48
99	41.69				41.49	41.72
100	42.10				41.84	42.20
101	42.46				42.21	42.68
102	42.83				42.63	43.12

Note. The differences in the last column ($v'=4$) are obtained from unresolved doublets.

The results are given in table 3. The final mean value of B_0'' is obtained by weighting each band according to the number of measured lines in it. Similar procedure gives us B_1'' , etc. Assuming a linear relation amongst the B' values we have

$$B_v' = B_e' - \alpha(v + \frac{1}{2}) \quad \dots\dots(5),$$

and applying the rule of least squares we have

$$B_v' = 0.08560 - 29.55 \times 10^{-5}(v' + \frac{1}{2}) \quad \dots\dots(6).$$

Table 3

Band	(2, 1)	(3, 1)	(4, 1)	(6, 0)	(8, 0)	(9, 0)
B'' (cm. ⁻¹)	0.10477	0.10472	0.10510	0.10566	0.10557	0.10559
B' (cm. ⁻¹)	0.08485	0.08449	0.08427	0.08385	0.08305	0.08273

Mean values

B_0''	0.105614 cm. ⁻¹	$r_{e''}$	0.7552×10^{-8} cm.
B_1''	0.104741 cm. ⁻¹	$r_{e'}$	0.8406×10^{-8} cm.
B_2''	$0.08560 - 29.55 \times 10^{-5}(v' + \frac{1}{2})$	D_0''	-2.573×10^{-8} cm. ⁻¹
B_e''	0.10605 cm. ⁻¹	D_1''	-2.508×10^{-8} cm. ⁻¹

Note. The value of B_1'' derived from column (4, 1) is 0.10510, and the value of B'_4 is 0.08427. Since the P and R branches are not separated in this band these constants have not been further employed although the value of B'_4 is inserted in figure 1.

§4. DETERMINATION OF BAND ORIGINS

It is possible to obtain a value for ν_0 from every line by use of the formulae

$$\nu_0 = P(J) - B'J(J-1) + B''J(J+1) - D'J^2(J-1)^2 + D''J^2(J+1)^2 \quad \dots\dots(7),$$

$$\begin{aligned} \nu_0 = R(J) - B'(J+1)(J+2) + B''J(J+1) - D'(J+1)^2(J+2)^2 \\ + D''J^2(J+1)^2 \quad \dots\dots(8), \end{aligned}$$

with the values for B and D already found. The values of ν_0 so obtained were reasonably consistent and simple averages were taken. The results for each branch of each band are given in table 4. The row $\nu_h - \nu_0$ gives the calculated distances of the heads from the origins by means of the formula $(B' + B'')^2/4(B'' - B')$ and we can thus give the calculated heads ν_h (calc.). The next row gives ν_h (obs.), the values for the heads actually observed by Rochester and Howell, whilst the final row gives the heads as calculated by them by the use of a least-square formula for all the heads of the A system. It will be noted that our analysis agrees more closely with these authors' calculations than with their separate observations.

Table 4. Band origins

	(6, 0)	(8, 0)	(9, 0)	(2, 1)	(3, 1)
ν_0, P	20318.17	20829.30	21084.88	18862.00	19120.90
ν_0, R	20318.67	20829.32	21083.44	18862.07	19119.80
ν_0 mean	20318.42	20829.31	21084.16	18862.04	19120.35
$\nu_h - \nu_0$	0.41	0.40	0.39	0.45	0.44
ν_h (calc.)	20318.83	20829.71	21084.55	18862.49	19120.79
ν_h (obs.)	20320.0	20832.3	21086.3	18863.0	19120.6
ν_h (calc.) R. & H.	20319.2	20830.4	21085.0	18862.2	19121.1

§5. ISOTOPE EFFECT

Lead has three main isotopes of masses 206, 207 and 208 having abundances 4, 3 and 7 respectively. Sulphur is relatively free from isotopes and has a mass of 32. Hitherto the isotopes of lead have only been identified in band spectra in the case of lead oxide⁽³⁾. Notwithstanding the relative abundance of the isotopes they were not obvious in the bands measured in the course of the present work, and it was only later that the weaker lines measured were so interpreted.

Taking ^{206}Pb as the isotope relative to the more abundant ^{208}Pb , we have for the ratio of the reduced masses

$$\rho^2 = ({}^{208}\text{PbS} \div {}^{206}\text{PbS}) = 1.001295.$$

Table 5. Isotope effect, all lines not included in table 1

(6, o)			(6, o)			(6, o)		
	δ	δ (calc.)		δ	(δ calc.)		δ	δ (calc.)
P 38	0.40	0.45	R 78	0.70	0.80	P 82	0.61	0.75
P 39	0.42	0.45	P 71	0.77	0.80	R 90	0.63	0.74
P 40	0.67	{0.45 0.90}	R 79	0.84	0.80	P 83	0.73	0.74
P 46	0.78	0.89	P 72	0.77	0.79	P 84	{0.72 1.57}	{0.74 —}
P 47	0.83	0.88	R 80	0.76	0.79	R 92	0.51	0.73
P 48	0.88	0.88	P 73	0.75	0.79	P 85	0.66	0.73
P 51	0.99	0.87	R 83	0.76	0.78	P 87	0.76	0.72
P 52	0.85	0.87	P 76	{0.70 1.46}	{0.78 —}	P 88	0.82	0.72
P 53	0.75	0.87	R 84	0.75	0.77	P 89	{0.67 1.48}	{0.71 —}
P 55	0.81	0.86	P 77	0.67	0.77	R 97	0.55	0.71
P 61	0.83	0.84	R 85	0.61	0.77	P 90	0.55	0.71
P 62	0.92	0.83	P 78	0.80	0.77	P 91	0.54	0.70
P 63	0.74	0.83	R 86	0.75	0.76	R 99	0.58	0.70
P 67	0.82	0.81	R 79	0.67	0.76	R 100	0.62	0.69
R 76	0.70	0.81	R 88	0.72	0.75	R 101	0.61	0.69
P 69	{0.80 1.40}	{0.81 —}	P 81	{0.74 1.41}	{0.75 —}	P 94	0.60	0.68
P 70	0.69	0.80	R 89	0.77	0.75	R 104	0.82	0.67

(8, o)			(8, o)			(8, o)		
	δ	δ (calc.)		δ	δ (calc.)		δ	δ (calc.)
R 54	0.49	0.60	P 65	1.02	1.14	P 81	0.51	0.54
P 52	0.56	0.60	R 74	1.10	1.14	R 89	1.09	1.07
R 60	{0.56 1.12}	{0.59 1.19}	R 75	{0.59 1.01}	{0.57 1.13}	P 83	0.54	0.53
R 61	0.98	1.18	R 76	0.62	0.56	R 92	1.05	1.05
R 62	{0.50 1.15}	{0.59 1.18}	R 77	1.04	1.12	P 85	0.52	0.53
P 56	0.53	0.59	R 78	1.03	1.12	P 86	0.50	0.52
R 65	1.06	1.17	R 80	1.08	1.11	R 95	0.97	1.04
R 67	1.03	1.17	R 81	1.01	1.11	R 97	0.94	1.03
R 69	1.15	1.16	R 82	1.04	1.10	R 98	0.47	0.51
P 62	0.55	0.58	P 76	0.54	0.55	R 100	{1.63 2.44}	—
R 70	1.08	1.15	P 78	0.60	0.54	R 101	0.93	1.00
R 71	1.05	1.15	R 86	{0.57 1.05}	{0.54 1.08}	P 94	0.46	0.50
P 64	0.45	0.57				R 102	0.57	0.50
R 72	1.16	1.15	R 87	1.08	1.08	R 103	1.76	—

Table 5 (cont.)

(9, o)			(9, o)			(9, o)		
	δ	δ (calc.)		δ	δ (calc.)		δ	δ (calc.)
R 51	0.71	0.70	R 73	0.71 1.57 1.94	0.66 1.33	R 90	0.55 2.99 3.79	0.62 — —
R 52	0.67 1.30	0.70 1.39	R 74	0.61	0.66	R 91	0.57 1.39	0.62 1.23
R 53	0.97	0.70	R 75	0.64 1.34 2.15	0.66 1.31	R 92	0.93 2.27	— —
R 55	0.55	0.69	R 76	0.63	0.65	R 93	1.27 2.41	0.61 —
R 56	0.65	0.69	R 77	1.21	1.30	R 94	1.19 2.10	1.22 —
R 57	0.68	0.69	R 78	0.56	0.65	R 95	0.62 2.35 2.78	0.61 — —
R 58	0.67	0.69	R 79	0.64	0.65	R 96	0.58 1.08 1.36	0.60 1.21 —
R 59	0.59 1.25	0.68 1.37	R 80	0.53	0.64	R 97	1.28 1.63 3.05	1.20 — —
R 60	0.62	0.68	R 81	0.61	0.64	R 98	1.40 1.90 2.40	1.20 — —
R 61	0.70 1.34	0.68 1.36	R 82	0.60	0.64	R 99	1.04 1.64 2.21	1.19 — —
R 62	0.75	0.68	R 83	0.58	0.64		2.79	—
R 63	0.69 1.30	0.68 1.36	R 84	0.70 2.70	0.63 —			
R 64	0.65 1.28	0.68 1.35	R 85	0.64	0.63			
R 65	0.55 1.25	0.67 1.35	R 86	1.43 0.67	1.26 0.63			
R 66	0.54 1.30	0.67 1.35	R 87	1.28 2.44	1.25 —			
R 67	0.67	0.67	R 88	0.50	0.62			
R 68	0.82	0.67	R 89	0.62 1.09 1.59	0.62 1.24 —			
R 69	0.55 1.11	0.67 1.35						
R 70	0.65	0.66						
R 71	0.61 1.27	0.66 1.33						
R 72	0.71 1.84	0.66 —						

As is well known, the isotopic shift can be regarded as the sum of two effects; (i) a bodily displacement of the whole band and (ii) a displacement of each line by an amount approximately proportional to its wave-number distance from the band origin. The first effect is given by

$$(\rho - 1) [(v' + \frac{1}{2}) \omega_v' - (v'' + \frac{1}{2}) \omega_v''] \quad \dots \dots (9),$$

and substituting for the ω 's and writing

$$v'' = 0, v' = 6, 8 \text{ and } 9$$

we have for the bands (6, o), (8, o) and (9, o) respectively shifts amounting to 0.960, 1.308 and 1.476 cm⁻¹, all positive. The second effect is negative and is given by

$$(1 - \rho^2) (\nu_0 - \nu) \quad \dots \dots (10),$$

where ν_0 is the band-origin and ν is the wave-number of the line in question. The result is that each line in the main P and R branches, if due to ²⁰⁸Pb, should have a line due to the isotope ²⁰⁶Pb on its more refrangible side, as above calculated, together with a line due to ²⁰⁷Pb midway between them and of a little lower intensity than that due to ²⁰⁶Pb.

In table 5 are given all the lines measured on the plates which remained after the main series given in table 1 for (6, o), (8, o) and (9, o) had been withdrawn.

The first column in the table gives the nearest *P* or *R* line on the red side of each of these extra lines; the corresponding wave-numbers have already been given in table 1. The second column, under δ , gives the amounts by which these new lines exceed in wave-number the corresponding lines in the first column, whilst the third column, δ (calc.), gives the corresponding displacements as calculated by the above formula with either ^{206}Pb or ^{207}Pb or both, as may be appropriate. It will be seen that the great majority of the remaining lines are thus satisfactorily accounted for. The extra lines in the tail of (9, 0) are probably due to the moderately strong band (10, 1) which occurs here. The fact that only a fraction of the isotope lines have been observed is probably due to a number of factors; for instance, the temperature of our absorption tube was kept down to an extent which was sufficient to show clearly the main structure of the bands with the minimum complication from overlapping bands. Thus the isotope lines recorded were quite faint and were just distinguishable from a very complex, though weak, background.

For the bands (2, 1), (3, 1) and (4, 1) the above formulae give results which are too small for us to be able to detect and throughout we have blends of all three lines.

The vibrational effect given by equation (9) is much greater for large values of v'' and small v' . In the (0, 7) band-head at $15,837 \text{ cm}^{-1}$ there is the further effect that over a considerable range the *P* and *R* branches are superposed so as to produce a simple spectrum and strong lines. The use of Rochester and Howell's values $\omega' = 261.1$ and $\omega'' = 428.14$ with equation (9) gives

$$\Delta\nu = -1.996 \text{ cm}^{-1}$$

The rotational effect given by equation (10) also is easily calculable. On examining a plate in the first order the isotopes were quite distinct and table 6

Table 6. Superimposed *P* and *R* lines in the band (0, 7) and their corresponding isotopes

$\nu (\text{cm}^{-1})$	$-\Delta_1\nu (\text{cm}^{-1})$	$-\Delta_2\nu (\text{cm}^{-1})$
15,694.69	1.00	2.05
91.63	1.18	2.07
88.48	1.01	2.21
85.14	—	2.26
81.95	1.15	2.32
78.65	1.08	2.28
75.34	—	2.04
72.01	1.04	2.14
68.53	1.13	2.07
65.18	1.11	2.09
61.58	0.96	2.05
58.08	1.06	2.14
54.54	—	2.26
51.02	—	—
47.46	—	—
43.82	1.10	2.09
Mean	1.08	2.15

$\Delta_2\nu$ applies to ^{206}Pb . $\Delta_1\nu$ applies to ^{207}Pb .

gives some measurements made. The rotational effect varies over the observed range uniformly from -0.18 to -0.25 cm^{-1} . The sum of the two effects as observed is entered for the two isotopes after each line. The mean effect for ^{206}Pb is seen to be double that for ^{207}Pb . The calculated mean value for ^{206}Pb is given by -1.996 cm^{-1} for the vibrational effect and -0.21 cm^{-1} for the rotational effect. The sum, -2.21 cm^{-1} , is in excellent agreement with the observed -2.15 cm^{-1} , since the formulae (9) and (10) are approximate and a small variation in the ω s would bring them into agreement.

Finally, the excellence of the various isotope results verifies the carrier as lead sulphide and confirms the vibrational analysis made by Rochester and Howell.

§ 6. ACKNOWLEDGEMENTS

We are indebted to Prof. W. L. Bragg, F.R.S., for the facilities placed at our disposal, to Prof. W. E. Curtis, F.R.S., for valuable criticism, and to Dr G. D. Rochester and Dr H. G. Howell for supplying us with much information not contained in their original articles.

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DEMONSTRATIONS

A LABORATORY METHOD FOR THE DETERMINATION OF THE PERIOD OF THE TRANSVERSE OSCILLATIONS OF FLEXIBLE RODS BY MEANS OF A PHOTOELECTRIC CELL. By G. A. BENNETT and J. E. CALTHROP, Queen Mary College

Demonstrated 28 January 1938

A UNIFORM bar of length l and of linear density m is rigidly clamped at one end and has a mass M suspended at the other. If I is the moment of inertia of the section about the trace of the neutral section, and E is Young's modulus for the material, the period T of transverse oscillations is given by

$$T = 2\pi \sqrt{\frac{(M + 0.24ml) l^3}{3EI}}$$

or

$$T^2 = \frac{4\pi^2 M}{3EI} + \frac{0.32\pi^2 ml^4}{EI}.$$

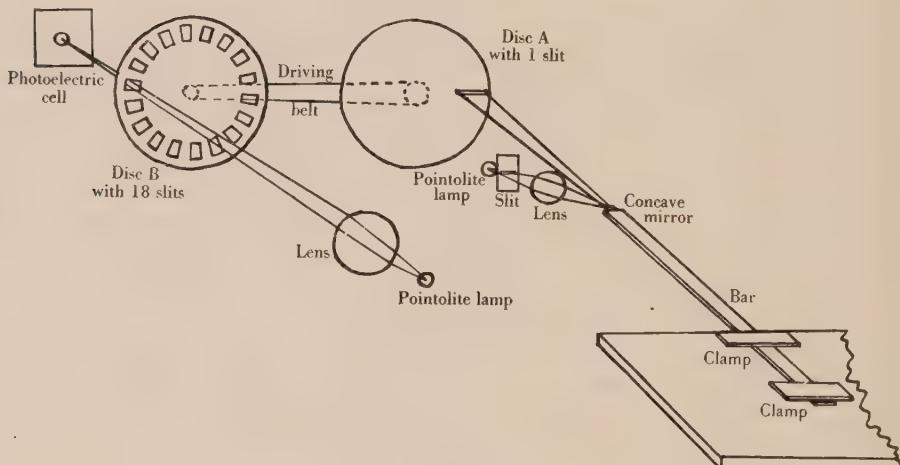


Figure 1

To verify this relation two experiments may be performed. (1) M is made equal to zero, l is varied, and T^2 is plotted against l^4 . (2) l is made constant, M is varied, and T^2 is plotted against M . The slopes of the expected straight lines should give a value of E .

In the method adopted for measuring T a slit is illuminated by light from a pointolite-lamp as shown in figure 1. By means of a lens the light is focused on a small concave mirror attached to the end of the vibrating rod, so as to give a sharp image on a distant ground-glass screen. In front of the screen is placed a rotating cardboard disc A provided with a single slit so that a steady central image is seen on the screen only when the period of the disc is equal to the period of the bar

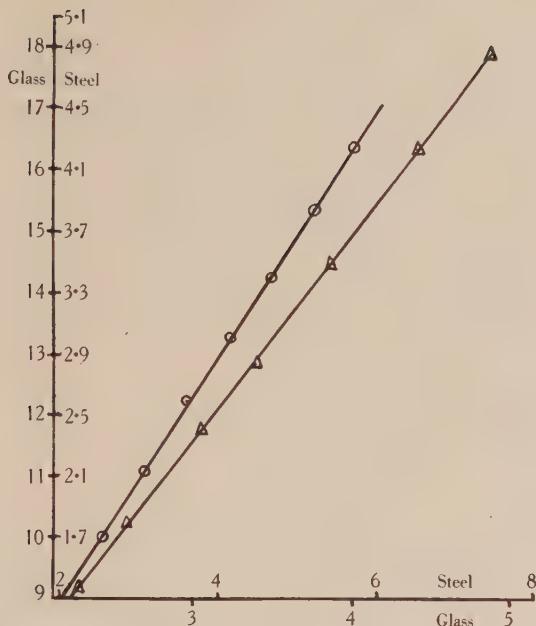


Figure 2



Figure 3

or some simple fraction of it. The rotating disc is geared to the axle of an electric motor, which is provided with another disc *B* having eighteen slits. Light from a pointolite lamp passes through these slits so that a photoelectric cell is illuminated intermittently. The cell is joined to a 2-stage or 3-stage valve amplifier, so as to produce in telephone receivers or a loudspeaker an audible note, the frequency of which is determined by obtaining beats with a sonometer wire. The gearing-ratio is found by replacing the disc having a single slit by one having thirty-six slits and illuminated so as to give an audible note in the photoelectric circuit. Thus if n is the frequency of the motor and x the gearing-ratio, the first disc gives a note of frequency $18n$ and the second a note of frequency $36n/x$. From the ratio of the corresponding lengths of the sonometer wire x is found. Figure 1 represents the arrangement of the apparatus. The diagram of the photoelectric circuit is omitted. Figure 2 shows a plot of l^4 and T^2 for steel and glass, and figure 3 a plot of M and T^2 for the same materials. The corresponding values of Young's modulus are as shown in the table.

Table. Young's modulus

Material	l^4 and T^2	M and T^2 (10^{12} dyne/cm 2)
Steel	2.09	2.075
Glass	7.28	72.5

The frequencies of the rods were of the order 10 to 20 c./sec.

SOME EFFECTS PRODUCED BY THE IRRADIATION OF LIQUIDS AND GELS WITH ALPHA, BETA AND GAMMA RAYS AND NEUTRONS.* By F. L. HOPWOOD and J. T. PHILLIPS

Demonstrated 11 March 1938

DURING an investigation of some of the effects of neutrons on substances of biological importance⁽¹⁾ it was found desirable to reinvestigate some of the effects due to alpha, beta and gamma rays which had been observed by ourselves and others in some cases before the neutron was discovered. The necessity for doing this arose in part from the fact that the only neutron-sources available for experiment emitted beta and gamma rays also. In the course of this work some phenomena were observed which appeared to be of sufficient general interest to bring before this society.

Decomposition of dilute solutions of hydrogen peroxide by gamma rays and neutrons. Figure 1 shows the action of gamma rays and neutrons on a dilute solution of hydrogen peroxide. The progress of the reaction was followed by means of standard chemical titrations.

The upper line (*A*) shows the combined effect of the neutrons and gamma rays from a mixture of beryllium and radium salt in breaking down the solution.

* A more complete description of some of these experiments together with a discussion of their quantitative aspects will be published shortly.

Line *B* shows the effect obtained from a strictly parallel control experiment using gamma rays only. Line *A-B* gives the effect due to neutrons as the difference of *A* and *B*.

All the graphs show a linear relation between the chemical decomposition and the amount of radiation absorbed and thus afford a basis for a chemical method of measuring the strength of a neutron source.

Liquefaction and regelation following irradiation of a gel. A small thin-walled glass capillary tube containing radium emanation (radon) is laid on the surface of a block of gel containing 6 per cent gelatine in water. The combined action of the beta and gamma rays causes the gel to liquefy locally, thus permitting the descent

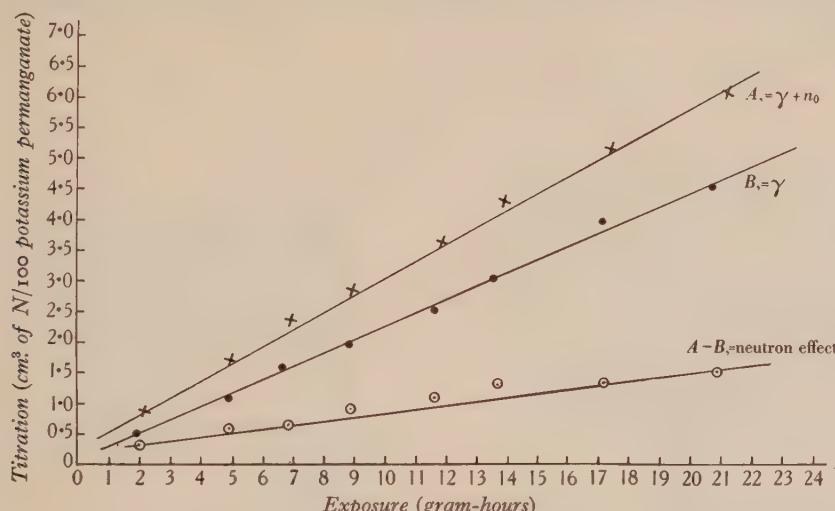


Figure 1. Neutron and gamma-ray irradiation of hydrogen peroxide. Concentration of solution, 0.63 g./l.; volume used for irradiation, 100 cm³; sources, *A*, 290 mg. of radium as chloride + 4.4 g. of beryllium; *B*, 290 mg. of radium as sulphate.

of the capillary tube. Following the descent, continued irradiation and interdiffusion between the liquid and unmodified gel results in regelation. Ultimately when the radon is "dead" the capillary tube is completely embedded in the gel (figure 2).

A similar tube filled with air remains on the surface of the gel.

Effect of gamma rays and neutrons on the formation of Liesegang rings. It was discovered by R. Liesegang⁽²⁾ that periodic precipitation of silver chromate will take place when a drop of silver nitrate solution is placed upon the surface of a glass plate covered with a shallow layer of gelatine impregnated with potassium bichromate. The precipitate takes the form of a disc surrounded by concentric coloured rings of varying thickness and diameter.

Contrary to the experience of others⁽³⁾, we have found that sufficiently intense irradiation of the gel during the formation of the rings causes marked changes in their structure. This can be seen in figures 3, 4 and 5. In some cases the effect is enhanced by the addition of a dye to the gel.

Developability of silver grains in a photographic emulsion when bombarded by alpha particles. It is well known that the energies of protons and alpha particles can be investigated by studying their ranges in photographic emulsions as indicated by the tracks of developable silver grains which they produce⁽⁴⁾.

Using this method, we have observed an anomalous effect when streaks of a solution of RaC, drawn by a rubber pen on a photographic plate, have been used as sources of alpha particles. In many cases two wide bands of tracks have been observed at one edge of a streak which are separated by a region practically devoid of them (figure 6). The absence of tracks in this region shows that, owing probably to some lack of neutrality in the solution, the silver grains cannot be made developable by alpha-ray bombardment, although alpha particles can be shown to be present in abundance. Evidence for this is afforded by the defect in formation of asters when many tracks originate at one spot. Figures 7 and 8 show a normal aster and an abnormal aster respectively.

Turbidity of irradiated protein solutions. As is shown by the increased turbidity of solutions after irradiation, many proteins are denatured by irradiation with alpha, beta or gamma rays. The addition of sodium chloride to a solution of egg albumen is said to enhance this effect⁽⁵⁾.

Figure 9 shows that the opposite effect can also occur.

Polymerization of unsaturated hydro-carbon compounds. It is well known that a number of chemical compounds can be polymerized by the action of ultra violet light, and the same effect is sometimes produced by alpha rays from radioactive substances^(6, 7).

We have found that styrene* and vinyl acetate† can be polymerized at room temperature by alpha rays, beta rays and gamma rays either acting in conjunction with neutrons or alone.

The polymerization is demonstrated by the increase in viscosity of the liquids, streaming polarization, and solidification.

* $C_6H_5 \cdot CH=CH_2$.

† $CH_2=CH \cdot O \cdot OC—CH_3$.

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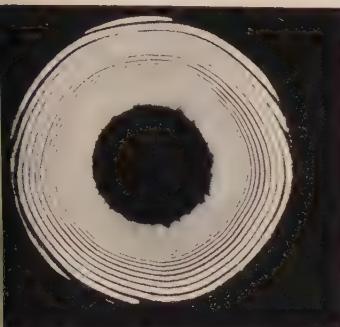


Figure 3. Normal Liesegang rings.

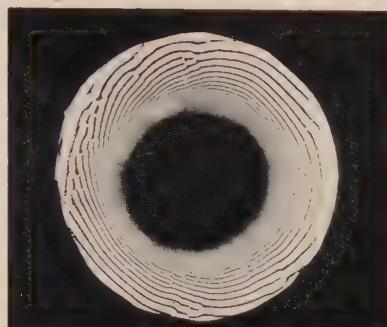


Figure 4. Liesegang rings irradiated with β and γ rays during period of formation.



Figure 5. Liesegang rings strongly irradiated with γ rays and neutrons during period of formation.



Figure 6. Region of non-developable silver grains separating areas of a photographic plate covered with tracks of alpha particles and protons.

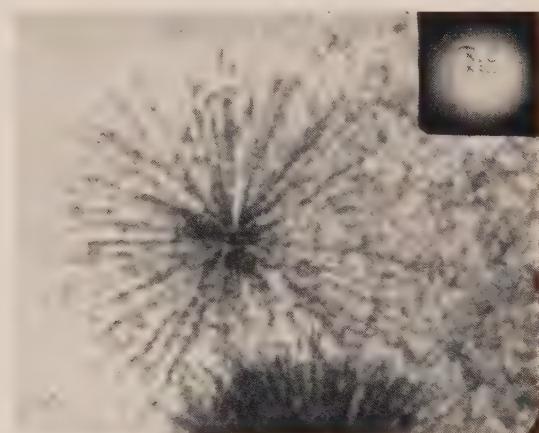


Figure 7. Aster formation of α -particle tracks on a photographic plate infected with radium C.



e 2. Capillary tube filled with
on, which has embedded itself
gel.



Figure 8. Defective aster formation due to non-developability of silver grains.

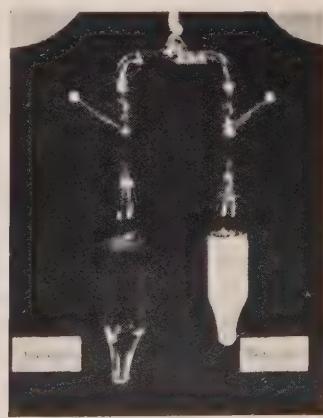


Figure 9. Solutions of egg albumen irradiated with full radiations from radon. The clear solution is identical in composition with the turbid solution, except that it contains some added sodium chloride.



Rutherford at Melbourne, 1925.

OBITUARY NOTICES

ERNEST, FIRST BARON RUTHERFORD OF NELSON, NEW ZEALAND, AND CAMBRIDGE

AUGUST 30, 1871—OCTOBER 19, 1937

M.A. New Zealand, 1893; B.Sc. and 1891 Science Scholarship, 1894; B.A. Research Degree and Coutts-Trotter Studentship, 1897; D.Sc. New Zealand, 1901; LL.D. Pennsylvania, Wisconsin, McGill, Birmingham, Edinburgh, Copenhagen, Glasgow; Ph.D. Giessen, Yale; D.Sc. Cambridge, Dublin, Durham, Paris, Oxford, Liverpool, Melbourne, Toronto, Bristol, Cape Town, London, Leeds; D.Phys. Clark; F.R.S., 1903. Macdonald Professor of Physics, McGill University, Montreal, 1898–1907; Langworthy Professor, University of Manchester, 1907–19; Cavendish Professor, University of Cambridge, 1919–37. Rumford Medal, 1905; Copley Medal, 1922; Barnard Medal, 1910; Franklin Medal, 1924; Albert Medal, 1928; Faraday Medal, 1930; Bressa Prize, 1908; Nobel Prize, 1908; Order of Merit, 1925; President of the Royal Society, 1925–30; President of the British Association, 1923; Guthrie Lecturer, 1927; President of the Institute of Physics, 1931–3; Knight, 1914; First Baron, created 1931.

§ I. EARLY YEARS IN NEW ZEALAND

Compiled by Prof. C. C. FARR, F.R.S., Canterbury College, Christchurch, New Zealand*

Lord Rutherford as a schoolboy. The following notes were drawn up by one of his sisters, Mrs Sergel, in consultation with another sister, Mrs Bell, and his mother, Mrs James Rutherford:

"He was one of twelve children, being the fourth child and second son of James and Martha Rutherford. He was always of a happy and loving disposition, besides being very unassuming in all his ways. In his holidays he was always willing to turn his hand to any little tasks, from painting the house to managing the rope-walk connected with the flax mill of his father. Also his fondness for music was very pronounced, his constant urging other members of the family to play and sing being in his opinion a pleasant accompaniment to his studies. One time he had a fad for taking photographs of his family, brothers and sisters, with a home-made camera, and he was continually taking clocks to pieces, evidently anxious to find out first hand the actual processes by which such a wonderful mechanism functioned. One of his chief physical interests was single-stick, which in his youth was a prominent exercise or physical-training method in secondary schools of his time. He found his skill particularly useful when he was made librarian at Nelson College, as he kept order with a wicket, and possibly his prowess as a swordsman instilled the necessary respect for authority. He was very fond also of making model water wheels, probably owing to the fact that nearly all the flax mills

* Part of the matter in this section has already been published in *The Times*. It is reproduced here by kind permission of *The Times* and of Prof. Farr.

which his father owned were working by means of water power. Mr Rutherford, senior, was particularly skilful in installing water mills, and the interest of the young student was naturally attracted to this form of mechanical movement. After passing one of his earlier examinations he was offered some position, which, however, he fortunately did not accept, deciding to continue his studies, although there is a suggestion that times were not very good for his parents, and the temptation to go early to earn money was therefore pronounced. However, wiser counsels prevailed.

"The reading of books was always a fondness of his. Anything at all seemed to interest him, even the very lightest of literature, something easy to follow, evidently forming a recreation to his mind. He was, however, specially fond of Dickens when young, and would welcome any opportunity to read out loud to younger members of the family, joining most heartily with his huge laughter, as it seemed to them, the various humorous incidents of *Pickwick Papers*. In holiday time he was often asked to teach his younger sisters, who in the ordinary way were instructed by a governess. In order to hold their attention or keep them quiet, he used to tie their pig-tails together. And when asked by his mother to teach the girls something he would generally reply, 'If they are mustered by nine o'clock, I will, but you must do the mustering.'

"Saturdays were often employed birds'-nesting, spearing eels in the river, catching brook trout in the pools in the bush, and long walks towards 88 Valley. And once when Rutherford was living at Havelock a hop-picking holiday was arranged. Mrs Rutherford, his mother, went to keep house at an old residence at Foxhill, for the four boys, Ernest, Jim, Herbert and Charlie. They earned about £13 in six weeks, picking hops. Ernest had a narrow escape while bathing during dinner hour in the Wai-iti river. He and one of his brothers were bathing and neither could swim. Ernest got out of his depth. Fortunately Jim just managed to reach him and get him out. It was kept a dead secret as otherwise bathing would have been stopped. Both boys were badly frightened. When the family moved to Taranaki, Ernest tried his hand at pheasants and wild pigeons. He used to get a horse and ride through the bush, often through deep mud, to reach the objective just as the sun was rising. There were three miro trees, the berries of which attracted the pigeons. They came in large numbers, but the ammunition was home made and the guns poor, so that he could not bring any down out of the high trees. The birds sitting on the high trees formed a very small target, until Ernest suggested a solution, and that was to fire when the birds were about to alight, which they would do with their wings outspread. On one occasion sixteen were bagged."

At Nelson College. The following notes were contributed by Mr C. H. Broad who was a schoolfellow of Rutherford at Nelson College, of which he afterwards became headmaster:

"Ernest Rutherford entered Nelson College as the holder of an Education Board Scholarship in 1887. He remained a pupil here for three years, gaining a University Junior Scholarship in 1889. He and I were in the fifth and sixth forms

together during the whole of his stay at Nelson College. I can well remember his arrival at the College. He had been placed by the headmaster, Mr W. J. Ford, in form V, an unusually high form for a new scholarship holder, and we, i.e. the gods of the fifth form, wondered who this fair-haired interloper was. We soon found out! During his three years' stay at the College he entered into the full life of the school in every way, games as well as study, and although he could never be described as an athlete he was nevertheless a forward in the first fifteen in his last year. What always particularly struck me about him was his extraordinary powers of concentration, even in the midst of the greatest turmoil. In the sixth form (not in school time of course) there was at times considerable uproar—books flying, etc.—and yet Rutherford would be absolutely oblivious to the confusion, his mind following up some mathematical point, geometrical rider, or the like. I am afraid some of us used to take full advantage of his abstraction in various boyish ways, banging him on the head with a book, etc., and then bolting for our lives. Another thing I well remember about Rutherford was his habit of strolling about with Dr W. S. Littlejohn on the half-holiday, up and down little-frequented streets near the College, Littlejohn drawing diagrams in the dust of Hampden Street and he and Rutherford discussing them. You could get a good deal of information from Dr Littlejohn, now Headmaster at Scots College, Melbourne, but at that time mathematical and science master at the College, to whom Rutherford owed so much of his early grounding in these subjects. It is interesting to note that in addition to mathematical prizes Rutherford also gained the Stafford scholarship for English history, the Simmons prizes for English literature, the senior classical prize and also the French scholarship, so that he was a boy of many parts. As far as I can ascertain, his academic successes while at school here were as follows: 1887, reading prize, Stafford scholarship for history; 1888, senior English literature scholarship, French scholarship, classical prize, form VI, and mathematics prize, form VI; 1889, Simmons prize for English literature, Latin prize, form VI, mathematics prize, form VI. As regards science, it has to be remembered that in those degenerate days chemistry was optional with French, and consequently Rutherford began his science late in his career here and then he was practically taken alone in physics and chemistry by Dr Littlejohn. Science has come into its own now, but in those days it was sadly neglected. Littlejohn, however, raised it to a very high standard in Nelson, but Rutherford was in the early stages of the process."

At Canterbury College. The following notes were drawn up by Mr R. M. Laing, M.A., a fellow undergraduate at Canterbury College at the time of Lord Rutherford's student days, with the help of Mr S. Page, B.Sc., who was Demonstrator in Chemistry and Physics to Prof. Bickerton during the same period:

"Rutherford came to Canterbury College in 1890 with a Junior University Scholarship. It was then a very small institution with some seven professors and 150 regular students. A laboratory for physics and chemistry was housed in a galvanized iron building, not much more than 60 feet long, under the control of Professor A. W. Bickerton. Mathematics was taught by Professor C. H. H. Cook.

To these two professors Rutherford naturally gravitated. They were of very opposite types. Professor Bickerton was heterodox in all his views, and very erratic in his methods of teaching, but at the same time highly original. He never gave out the formal thoughts of another, but expressed everything in his own terms and from his own point of view. He had no knowledge of mathematics, but worked out his mechanical and physical problems by graphic methods, when graphics were scorned by the more orthodox professor of mathematics, and before they had obtained the position they now have in physical science. He had wide and far-reaching views on the evolution of the universe, and though these views have not in the main been confirmed by subsequent research, yet amongst them were some novel ideas which have since been established by astronomical physicists. Though Professor Bickerton's teaching may have been of little value for the dull student in many ways it suited Rutherford's type of mind. Bickerton was an enthusiast for research and had the power of making others share his enthusiasm. When most men thought that physics had reached an *impasse* beyond which it could go no further, he believed that it was only at the beginning of world-shaking discoveries, and though his reasoning may have been crude, yet his conclusion was correct and has since been amply justified. Naturally such a professor filled Rutherford with love for his work, and taught him to break away from the trammels of the hide-bound physical science of the day. For students of some individuality Professor Bickerton was an excellent stimulant, even though he did not by any means keep himself abreast of the developments of his own day and time. On the other hand, the mathematical professor, C. H. H. Cook, thoroughly orthodox in all his views and strictly scholastic in his methods, and within his limitations a very able man, applied the brake to the young student and prevented his speculations from leaving the ground of fact. Here Rutherford obtained a sound instruction in the mathematics of the day, with which he was able to control the wilder flights of his physical teacher.

"Rutherford came to Canterbury College a boyish, frank, simple and very likeable youth, but with no precocious genius. Two others of his contemporaries at least were regarded by his teachers as equal to himself in ability and brilliance, but these have not distinguished themselves as he has done. The secret of Rutherford's success has been that once he saw the goal he turned neither to the right hand nor to the left, no matter how fascinating the byways might appear, but went straight on to the central problem of his research, the structure of the atom. No doubt in his earlier papers he was groping for a pathway, but as we shall see it was soon found and has never been left; and his whole progress has been one long story of increasing success. He appears as No. 338 in the register of students of Canterbury College, and his career there is thus described (*History of Canterbury College*, 1927, p. 203): '1890, Exhibition in mathematics; 1891, exhibition in mathematics; 1892, exhibition in experimental science and mathematics; 1893, B.A., senior scholarship in mathematics; 1894, 1st class honours, mathematics, and 1st class, physical science; 1894, 1851, Exhibition science scholarship in electricity; 1901, D.Sc. (N.Z.).' Now the 1851 *Exhibition Scholarship* was awarded once in about

three years to the New Zealand student showing most promise in some branch of science, and enabled him to go to an English university and carry on his studies there.

"For his thesis in physics, Rutherford had carried out an inquiry into the magnetization of iron by high-frequency discharges. This research was done in a miserable, cold, draughty, concrete-floored cellar, which was usually known to the students as the 'Den', and in which they were accustomed to hang up their trenchers and gowns. There was no other accommodation available. This Den will surely be historic in future. Rutherford's investigation—his first paper—is published in the *Transactions of the New Zealand Institute*.^{*} The first paragraph of the paper is as follows: The subject of the magnetization of iron in very rapidly varying fields has been touched upon more or less fully by different scientists, notably Dr Lodge, Professor J. S. Thomson, Hertz, and a few others. In Dr Lodge's *Modern Views of Electricity* we find the following: 'But in the case of a discharge of a Leyden-jar iron is of no advantage. The current oscillates so quickly that any iron introduced into the circuit, however subdivided into thin wires it may be, is protected from magnetism by inverse currents induced in its outer skin, and accordingly does not get magnetized, and, so far from increasing the inductance of the discharge circuit, it positively diminishes it by the reaction effect of these inducted currents; it acts, in fact, much as a mass of copper might be expected to do.' Rutherford was able to show, in opposition to the prevailing scientific opinion of the day, that iron is strongly magnetic in rapidly varying fields, even when the frequency is over 100,000,000 per second. It is obvious that in those days to carry out such an investigation required high powers of experimentation in order to deal with frequencies of such an order. In fitting up his apparatus Rutherford received considerable assistance from Mr S. Page, the demonstrator in the laboratory. This is not the place to discuss the details of the experiment; but suffice it to say that for magnetization purposes needles were used which ranged in diameter from 0·1 in. to less than 0·01 in. For lower rates of oscillation ordinary piano wire was used; but when the rates of oscillation were of the order of 10^{-8} per second a more delicate detector was required. This induced Rutherford to consider the dumb-bell oscillator of Hertz. The use of this detector led naturally to the study of the Hertzian waves, as they were then termed. Rutherford's second paper published in the following year† was entitled 'Magnetic viscosity'. In order to investigate small intervals of time, Rutherford invented a time apparatus which was capable of measuring intervals up to 0·00001 sec., a remarkable degree of precision considering the crude apparatus with which he had to work. The time was measured by the space through which a body making and breaking contact fell, and careful and minute corrections were made to ensure accuracy. By this time Rutherford was able to send Hertzian waves from one end of the old 'tin shed', as it was called, to the other, and pick them up by means of a detector of his own invention. Thus he was started on a career for the investigation of radiations that led him to an explanation of the radio-activity of radium, when other investigators were baffled by the phenomena there presented.

* *Trans. N.Z. Inst.* 27, 481 (1895).

† *Trans. N.Z. Inst.* 28, 182 (1896).

"But Rutherford's whole time was naturally not taken up by his researches. He was a normal healthy student amongst other students. In the outdoor world he held his own at least. The chief field sport of those days, as it is still at Christchurch, was rugby football. Rutherford played in the first fifteen of Canterbury College as a forward, though without any particular distinction. On the whole he was of a conservative type of mind, though very fond of discussion. With fellow students he would sometimes discuss till the small hours of the morning the writings and personalities of such authors as Tennyson and George Sand, who were much in vogue then. Further opportunities for discussion came with the establishment of a Science Society among the students. Some of the more radical of the students thought that scientific topics were not given a fair and full hearing in the community and that it would be an excellent thing for education in the University if some group could be formed to discuss what in those days were considered advanced forms of thought. With this end in view a Science Society was formed in 1891. Rutherford was one of the original members, and amongst its founders was the late Mr W. G. Pye, a man of broad philosophic thought and full of ideas then considered heterodox. One of his heresies was that the atoms could not be discrete particles, but that there must be some more fundamental form of matter, more primitive even than the atom. Consequently the first subject for discussion was the evolution of the elements. Thus early was Rutherford led to consider the possibility of subatomic structure. Other subjects considered were, evolution in biology, evolution in psychology, evolution in morality and religion. Now in Christchurch at that time it was considered scarcely respectable to believe in evolution, and the University community was rather shocked at the open discussion of such subjects by young students. Rutherford himself felt that we had gone rather too far, and was with difficulty persuaded to take the secretaryship of the Society in 1893. In 1894 he read a paper on the then new subject of electrical waves and oscillations. The following is the note in the minute book of the Society on the address: 'Mr Rutherford then read his paper on electrical waves and oscillations, in which he dealt with oscillatory discharges in general, referring more particularly to the recent researches of Hertz and Tesla and their bearing on Maxwell's theory. The paper was very fully illustrated by experiments performed by Mr Rutherford with the assistance of Mr Page and Mr Erskine, the most striking of the experiments being a reproduction on a small scale of Tesla's experiments on the rapidly alternating currents.' Thus early had Rutherford embarked upon the course of Wordsworth's Happy Warrior,

the generous Spirit, who, when brought
Among the tasks of real life, hath wrought
Upon the plan that pleased his boyish thought;
Whose high endeavours are an inward light
That makes the path before him always bright,
Who, with a natural instinct to discern
What knowledge can perform, is diligent to learn.

a course from which he did not depart throughout his career."

On the staff of the Boys' High School, Christchurch. The following notes are by Mr O. Gillespie, who was a pupil when Lord Rutherford was a master at the Boys' High School, Christchurch. The Mr Walton mentioned is another old master, now dead:

"Lord Rutherford is with me a dim but very delightful memory. He endeavoured to teach mathematics to a form of boys to which I belonged. He certainly made no impression on me and I am doubtful whether his unique methods were any use to the ordinary monkey-minded schoolboy. He was, of course, entirely hopeless as a schoolmaster. Disorder prevailed in his classes, not quite so overt as the Auckland riots but far more continuous. I do not remember myself following any one of his intellectual processes on the blackboard, the medium through which he endeavoured to illustrate them. They were done like lightning. When he detected some more than usually noisy boy he sent him sternly for the Appearng Book. All the lad had to do to escape the consequences of his misdeeds was to stay out of the class room long enough for Rutherford's enormous mind to have bulged in some other direction, and sneak back to his seat, when he would inevitably not be noticed. Rutherford had the quite modern theory too of giving the boys the Answer Books, observing that the working was what really mattered. I am afraid, though, that he did not really too carefully inspect the working as I got quite good marks personally by filling in the answer correctly and working back a mere mass of x s, y s etc., which were put in more for their decorative effect than anything I understood about. The main characteristic of the mob mind of a schoolboy class is its ape-like cunning, and we certainly had him added up as a genial person whose interests had nothing to do with the keeping in order of small boys. He used to blurt suddenly into anger which was succeeded by a sort of desperate calm. This latter mood was hailed with real joy by all pupils. I remember one pupil very well, though I cannot remember his name, who was dealing with the problem of proportion. The questions and answers were something like these (mind you this is only a shadowy memory) but I remember that even my very defective mathematical fatuity saw something comic in the argument. The sum was something like this: If 9 horses plow 28 acres in 16 weeks how long will it take 5 horses to plow 11 acres. The pupil being cross examined divided by the number of horses and Rutherford explained that five horses would take longer than nine and that, therefore, the days required should be multiplied. The pupil simply said, 'Mr Walton said we had to divide and I am going to divide.' Rutherford simply dropped his pencil and looked hopeless. I am afraid as a schoolmaster he would have been a very bad misfit as First Assistant at Fernside or Cust. This, of course, is to his eternal credit. My recollection is that we all liked him personally immensely."

§ 2. RUTHERFORD WHEN A RESEARCH STUDENT AT CAMBRIDGE

By Sir J. J. THOMSON, O.M., F.R.S.

My friendship with Rutherford began in October 1895 when he came up to Cambridge University as a Research Student and began at once to research at the Cavendish Laboratory. Before that time, in addition to our own students who began research after taking their degree, there had been professors and teachers at other universities who spent their Sabbatical Year in research in the Cavendish Laboratory. These were not members of the University and their work did not receive any recognition from it. In 1895 a regulation came into force by which graduates of other Universities could come up to Cambridge and become members of the University, and if after two years' residence they submitted a thesis which was declared by the referees to be of distinction as a record of original research they were enabled to receive the degree of M.A. Rutherford was the first to take advantage of this regulation, though he was only a few minutes ahead of J. S. Townsend. Rutherford was a graduate of Wellington College, New Zealand, and came over with an 1851 Exhibition. He was at that time 25 years of age, a fine, stalwart, impressive man, and he had not been more than a few weeks in the Laboratory before it was evident that he was a man of great determination and driving power. He did not require any suggestions as to the kind of research he should take up at the Laboratory, as the great majority of research students do; he brought with him his own problem which he had begun before he left New Zealand; this was an instrument for detecting wireless waves. In those early days of wireless telegraphy such instruments were neither sensitive nor very reliable. This was not altogether due to the small energy in the waves, but arose partly from the fact that the electric currents they produced in the detector were altering their directions millions of times per second. Rutherford's detector was one in which the currents going one way produced no effect while those going the opposite way did. If a piece of soft wire is magnetized to saturation, then when it is placed inside a coil through which electric currents are flowing, those flowing in one direction will not affect the magnetization while those going in the opposite direction will do so. As these experiments on wireless communication required observations to be taken simultaneously at two places, it was necessary to have at least two observers and the transport of the instruments from place to place required organization. Rutherford surmounted these difficulties by enlisting the services of his friends, and was so far successful that at one time he held the record for long-distance wireless telegraphy, having detected at the Laboratory signals which came from the Observatory about 2 miles away. An account of these researches was published in the *Transactions of the Royal Society*, vol. 189. He had not been in the Laboratory more than a few weeks before I became convinced that he was a physicist of exceptional promise, energy and strength of character. During his stay in Cambridge he was awarded the Coutts Trotter Studentship in Trinity College; it is awarded without examination, and the



From a photograph by Stearn, Cambridge

Research Students, 1899

E. B. H. Wade	G. A. Shakespear	C. T. R. Wilson	E. Rutherford	W. Craig-Henderson	J. H. Vincent	G. B. Bryan
J. McClelland	C. Child	P. Langevin	J. J. Thomson	J. Zeleny	R. S. Willows	H. A. Willis
						J. S. Townsend

electors are instructed to pay more regard to the promise of power to carry on original research than to the amount of work already done.

Whilst Rutherford was working at his wave-detector, X rays were discovered. As soon as the discovery was announced I had a copy of Röntgen's apparatus made for the Laboratory and the first thing I did with it was to see if the X rays would make a gas through which they passed a conductor of electricity. To my great joy I found that they did even for the smallest electric forces. For more than ten years, experiments on the conduction of electricity through gases had been going on in the Laboratory, but the only way to get the electricity through the gas was to use very large electric forces and get electric sparks or to use flames; both these methods were exceedingly capricious. The X rays gave a very convenient and reliable method of making the gas a conductor. The method seemed so promising that a large number of the research workers in the Cavendish Laboratory were making experiments on this subject. Rutherford devised methods of great ingenuity and reliability, which he carried out with superb experimental skill, for determining the fundamental quantities connected with the subject, and he obtained very valuable results which helped to make the subject of conduction through gases metrical whereas before this work had been only descriptive.

Rutherford had the good fortune to begin his career as a physicist at a time perhaps unprecedented in physical discoveries of fundamental importance. A few months after the discovery of X rays, H. Becquerel found that uranium and its compounds gave out radiation which could pass through substances opaque to light, could affect a photographic plate and travelled in straight lines from its source. Shortly afterwards Schmidt found that thorium, the element next in atomic weight to uranium, possessed the same powers, but the most important discovery of all was that made by M. and Madame Curie, who discovered the new element radium which possessed these powers to an enormously greater degree than either uranium or thorium. Substances possessing these properties are said to be radioactive. The radiation was not all of the same kind, there was one kind which had comparatively small powers of penetration compared with the others; it was thought not to be deflected by magnetic forces, though Rutherford showed afterwards that it was so to an extent not comparable with the deflection produced in another type of radiation; while there was a third type of radiation which was not deflected at all by magnetic force. In 1899 Rutherford began a careful study of the three types of radiation, which he called the α , β and γ radiations, a notation which is used to this day. He began with uranium; the results he got were interesting but there was nothing fantastic about them—if you got a result one day you could get it the next. Then he took up thorium and found a very different state of affairs; it seemed as if the only results to be got were those that had never occurred before. Its behaviour seemed to be entirely frivolous, it was not affected by raising it to high temperatures or bombarding it with radiation from other radioactive substances, while opening the door of the work room produced enormous changes. Its radioactivity seemed to be contagious and infected other solid bodies in its neighbourhood. Rutherford left Cambridge in 1898 to become Professor of Physics at Montreal

and resumed his experiments on thorium. These led him to a discovery of fundamental importance, which was the origin of modern views of the processes going on in radioactive substances. The discovery was that thorium gives out not only radiations but a radioactive gas which he called an emanation; this may be wafted about, and if it settles on solid bodies makes them behave as if they were radioactive. The emanation is not permanent but after a time turns into a substance which is not radioactive. It is a very striking example of the wisdom of the policy of not leaving behind you in a research things which seem irrational according to current views.

Rutherford left Cambridge for Canada before he was eligible to sit for a Fellowship at Trinity, but when he returned to Cambridge as Cavendish Professor the College took the first opportunity of securing him as a Fellow.

§ 3. RUTHERFORD AT MCGILL UNIVERSITY

By A. NORMAN SHAW

It was fortunate for McGill University, after the departure of the brilliant Hugh L. Callendar in 1898, that John Cox, the Director of the Macdonald Physics Laboratory, was wise enough to choose Rutherford for the vacant chair. Thus at the age of twenty-seven Rutherford came to McGill University as Macdonald Professor of Physics, at about the age at which J. J. Thomson was appointed to the Cavendish chair.

The story of Rutherford's researches at McGill is one of the most impressive chapters in the history of science. Exhibiting that remarkable flair for choosing the best path to discovery, which characterized his work throughout his life, Rutherford seized on the problem of the radiations from compounds of uranium and radium. While the Curies concentrated on the chemical problems of isolating radioactive substances and determining their properties, Rutherford sought for methods of definite measurement which would reveal the physical character of the new phenomenon, and supply quantitative data concerning the behaviour of the radiations and the atoms which emitted them. In nearly all his investigations he devised ingenious direct measurements that would provide, and also test indisputably, new steps in the formation of a clearer picture or model of atomic structure and behaviour.

Throughout his life he viewed with considerable impatience the growing tendency to replace simple theoretical models or pictures and their experimental testing by an elaborate analysis and procedure designed to be as much as possible independent of all preconceived ideas. He believed that this tended to introduce unnecessary philosophical problems and difficulties, and he doubted whether a strict adherence to this procedure would be justified by greater success either in resolving obscurities of theory or in obtaining new knowledge and its fruitful application. By direct experimental attack Rutherford was able quickly to outline a simple picture concerning the new radiations. In 1899 he announced that the

radiations from these substances were of three types, which he called alpha, beta and gamma rays.

The prolific investigations on the properties of these radiations yielded a wealth of data. With the aid of pupils and collaborators, who were soon attracted from centres as far apart as England, the United States, France, Germany and Poland, papers poured out of the Macdonald Physics Laboratory for several years at the rate of nearly one a month. Of those who were attracted from abroad, many will remember Soddy, Hahn, Levin, Godlewski and Rumelin, each of whom returned to his respective country with seeds for further development and new knowledge to spread.

It was Frederick Soddy, soon to become an authority on the chemistry of the radioactive elements, who in 1903 joined with Rutherford in the brilliant unfolding of the general theory of radioactive disintegration. The constant production of fresh radioactive matter by all radioactive materials and the subsequent decay of its radioactivity, were shown to be due to the spontaneous disintegration of atoms, proceeding according to the laws of chance at such a rate that the radioactivity of a given product at any time was always proportional to the number of atoms which remained unchanged at that time. A mass of disconnected facts was soon welded into a homogeneous whole, and the evolution of whole series of radioactive substances, often differing from the parent elements in their chemical properties, was explained both qualitatively and quantitatively. Among others working actively with Rutherford at this time were H. T. Barnes, A. S. Eve, H. L. Bronson, D. McIntosh, R. B. Owens, R. W. Boyle, H. L. Cooke, R. K. McClung and Miss H. Brooks, members of the McGill staff who each made important contributions in this fascinating new field. The ability with which Rutherford got the maximum amount of work from all those around him, and at the same time imparted to them a measure of his own enthusiasm rapidly became noted, and almost every corner of the Physics Laboratory developed into a hive of continuous activity.

The important measurements of the heating effects of the new radiations were made with the collaboration of H. T. Barnes, who later occupied the Macdonald chair vacated by Rutherford, and afterwards became Director of the Laboratory (1909 to 1919). Rutherford always showed a keen interest in the well-known work on ice which Barnes was developing at that time. When Rutherford came to Montreal, Barnes was one of his first friends, and with the kindly and scholarly John Cox, who was Director of the Laboratory throughout Rutherford's period here, assisted him in his adjustments to routine duties at McGill and to the ways of our undergraduates. About 1904, A. S. Eve, afterwards another holder of the same chair and then Director of the Laboratory from 1919 to 1935, became one of the most active of Rutherford's research associates. Over twenty-five references to his work at this time are given in Rutherford's standard treatise on *Radioactivity*. Here again a warm personal friendship was established which lasted till the end of Rutherford's life.

The additional support Rutherford obtained at McGill from Sir William Macdonald in the purchase of radium and his presentation of a liquid air machine,

must not be forgotten in reviewing the conditions which made all this new work possible. In addition to the essential talent in the man, great discovery requires provision for freedom of action and protection from time-consuming routine, but without the radium and the new experimental weapons progress in this field would have been impossible. The contribution of John Cox in supporting Rutherford to the utmost and relieving him from routine, and that of Sir William Macdonald in providing first the Laboratory, second the chair, and third the special equipment, were essential factors without which the whole story would have been impossible here. The returns from these policies and investments have been truly magnificent!

To proceed with the story—to “get on with it”, as Rutherford would so often shout at the least sign of delay or interruption—the liquid-air machine enabled him to be the first to condense radium emanation (radon) and study its products and their properties. Without liquid air the production of the high vacua needed for many experiments would have been impossible at that time. Liquid air itself was a great novelty then, and in addition to its use in low-temperature work it provided the material for many entertaining demonstrations and lectures which were very popular in Montreal. Almost everyone from the Director to the janitor seems to have given liquid-air demonstrations during this period. On one occasion when liquid air was required—and it took over an hour to make a litre then—Rutherford found that the prepared supply had been taken to a church social for a demonstration, with the immediate result that the strains of “Onward, Christian Soldiers” ceased in the professor’s laboratory for some hours.

The discovery of radium A, B, C, D, and E; the discovery of radiothorium by Otto Hahn, who joined Rutherford to obtain guidance in the study of the thorium family; the early work with what turned out later to be cosmic rays, undertaken by H. L. Cooke; the measurement of the age of radioactive ores from their helium and lead content; the first studies of the collisions of alpha particles with atoms, and their resultant scattering, the beginning of the use of alpha particles as exploratory projectiles for the invasion of the atom; and experiments on ultra-violet radiations and numerous applications of the new sub-atomic physics, all added to the mountain of new material for the first edition of Rutherford’s *Radioactivity*, by far the best of his books, and to the steady stream of papers which continued till he left for Manchester in 1907.

When Rutherford was working on the detection and isolation of the numerous members of the radium family and developing the theory of the disintegration of matter, there were several occasions when colleagues in other departments gravely expressed the fear that the radical ideas about the spontaneous transmutation of matter might bring discredit on McGill University! At one long-remembered open meeting of the McGill Physical Society he was criticized in this way and advised to delay publication and proceed more cautiously; this was said seriously to the man who has probably allowed fewer errors to creep into his writings, and found it less necessary to modify what was once announced, than any other contemporary writer. At the time he was distinctly annoyed and his warm reply not entirely adequate, for in his younger days he sometimes lost his powerful command of

ready argument when faced with unreasonable or uninformed criticism. Immediately John Cox quietly rose to his support, and gave a clear review of the new ideas. Cox not only revealed incidentally his own grasp of the validity and significance of Rutherford's discoveries, but ended rhetorically with a stirring prediction that the development of radioactivity would bring a renown to McGill University by which in the future it would be widely known abroad. He ventured also to predict that some day Rutherford's experimental work would be rated as the greatest since that of Faraday—an opinion now held by the majority of those competent to judge.

The McGill Physical Society, which has been active without interruption since 1897, reached its greatest heights in Rutherford's day. The announcement of each discovery of importance was first heard there. The frequency of these discoveries, the brilliancy of the work, and the quality and value of the discussions, impressed all comers. It was there that Rutherford developed rapidly as a speaker, and after the first few years was to be heard and seen almost at his best. His clarity and direct use of simple language were coupled with dynamic ardour and contagious enthusiasm, so that even those who were unable to keep pace with the technical aspects of the subject were delighted and spellbound listeners.

Witness for example the reactions of the eloquent John MacNaughton, Professor of Classics, who has shot many a satiric dart at scientists and their doings—"plumbers" and "destroyers of art" he has sometimes called them—but Rutherford seems to have captured him in one lecture. He wrote as follows, in the *McGill University Magazine* for April, 1904: "... We paid our visit to the Physical Society. Fortune favoured us beyond our deserts. We found that we had stumbled in upon one of Dr Rutherford's brilliant demonstrations of radium. It was indeed an eye-opener. The lecturer himself seemed like a large piece of the expensive and marvellous substance he was describing. Radioactive is the one sufficient term to characterize the total impression made upon us by his personality. Emanations of light and energy, swift and penetrating, cathode rays strong enough to pierce a brick wall, or the head of a professor of literature, appeared to sparkle and coruscate from him all over in sheaves. Here was the rarest and most refreshing spectacle—the pure ardour of the chase, a man quite possessed by a noble work and altogether happy in it."

When the assurance is recalled with which Rutherford discussed the major problems of physics in learned societies, and the ability with which he handled men, it is surprising to remember that as a young man he was a nervous lecturer, particularly when dealing with elementary topics for undergraduates. His lectures on electricity and magnetism to large classes of second-year engineering and arts students at McGill were at first above the heads of the students, and revealed a feeling of despair in regard to the previous mathematical and scientific training of his class. Those of his students who were interested in physics, however, caught something of the fire with which he inspired all his advanced students and collaborators. They learned the importance of striving to build their knowledge on fundamental principles established by experiment and to achieve the ability to

apply these principles and to reason about them. Any attempts to concentrate mainly on definitions and isolated facts, and to rely primarily on memory, he roundly condemned. His scorn at the memorizing of electrical formulae, imagined by many students then as now to be a necessary part of the process of learning, will never be forgotten by students in his classes who pinned their faith on memory.

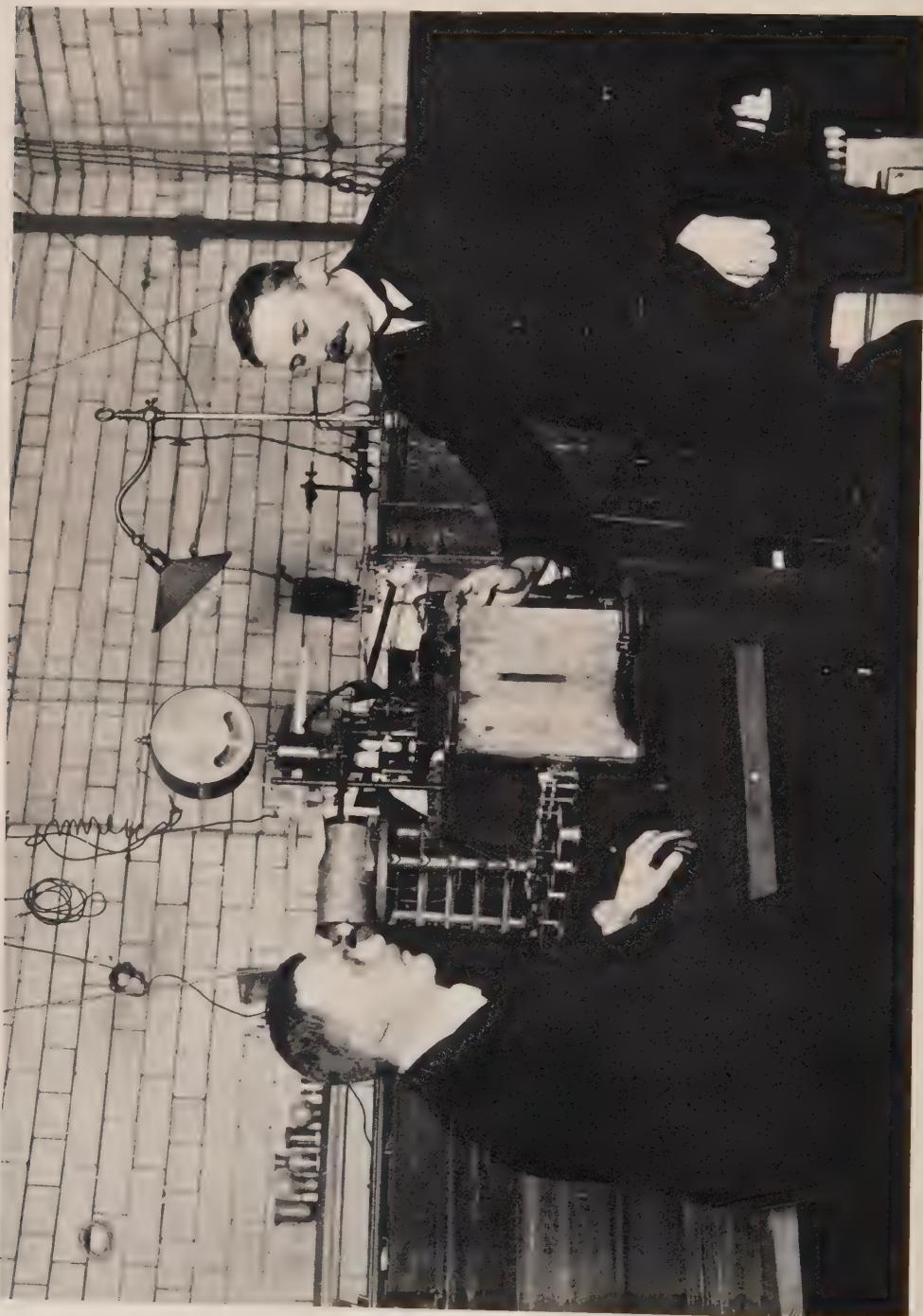
Before he left Montreal in 1907, at the age of thirty-six, he had already been elected Fellow of the Royal Society of Canada (1900) and Fellow of the Royal Society of London (1903), awarded the Rumford Medal (1904), appointed Bakerian Lecturer at the Royal Society (1904) and Silliman Lecturer at Yale (1905), elected President of Section III in the Royal Society of Canada (1906), and received honorary degrees from the universities of New Zealand (1901), Pennsylvania (1906), Wisconsin (1906) and McGill (1907). Before leaving he had already been slated for the Nobel Prize in Chemistry (\$40,000), which was awarded to him in 1908. He was given the chemistry award because the Nobel Committee classified the new phenomena of atom-changing as chemical by definition.

The debt of Canada to Lord Rutherford is beyond assessment. Undoubtedly the greatest outburst of original discovery that has occurred in Canada was entirely due to his leadership. Its subsequent influence affected all walks of science in the country, speeding the growing demand for higher scientific training and investigation. For almost the first time, Canadians began to understand that the scientific developments of modern civilization had been made possible primarily by workers and thinkers of the Rutherford type. The methods of scientific thinking and procedure attracted more attention as an immediate result of his spectacular achievements, and the vital demand for more research and scientific method in universities, in industry, and in national enterprises was greatly strengthened. The standards of our youthful Canadian Royal Society, the quality of scientific work in government departments, and the conduct of higher training in our universities were in turn the targets of his constructive criticism, for in spite of his indefatigable labours in the laboratory, he rarely missed an opportunity to promote the spread of science and its methods of thought and procedure.

§ 4. RUTHERFORD IN MANCHESTER, 1907-1919

By Prof. H. R. ROBINSON, F.R.S.

Rutherford, as Langworthy Professor of Physics and Director of the Physical Laboratories, served the Victoria University of Manchester for nearly twelve years, and these, in spite of the abnormal conditions of the last five of them, were among the most fruitful years of his scientific life. The work he did in these years has long been incorporated in the standard literature of physics, and it will be familiar, at least in outline, to all readers of these *Proceedings*, even to those who have not specialized in radioactivity or its later development, nuclear physics. There is therefore no point in attempting here a detailed survey of his scientific work in Manchester; no more is needed than a very brief account, sufficient to show which



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of Rutherford's major contributions to science were associated with the Manchester laboratory, and to indicate the main features of the work which he did and directed there. Similarly, no attempt will be made to mention by name all the members of the research school which he built up in Manchester in the years before the War. I found it easy to write down from memory more than 40 names of workers belonging to that period; in what follows, only a few of these names will be mentioned and these will not necessarily be the most important ones. It must be understood that many of those omitted are at least as distinguished as many of those included; in fact, with better cause than Ruy Gomez, I am compelled to say "J'en passe, et des meilleurs". On the other hand, the more personal and—if we may so call them—the more domestic details of Rutherford's life in the Manchester laboratory are not to be found in the scientific literature; an attempt—necessarily incomplete and one-sided—will therefore be made in the following pages to recapture some of these.

Almost immediately after he arrived from McGill, Rutherford began, with Geiger, the beautiful and now classical experiments in which individual α particles were detected by their electrical effects. The results of this work, in which in effect an almost direct count was made of the number of α particles emitted per second by a gramme of radium, were published in 1908. From them it was possible to calculate a number of important constants, and when they were combined with the known rate of production of helium gas in radium salts, they yielded the most direct determination imaginable of Avogadro's number. At the same time, Rutherford and Geiger measured the total charge carried away in a given time by the α particles from a radioactive source of known strength. By combining this result with that of the counting experiments they were able to show that the α particle was doubly charged, and to deduce a trustworthy value for the electronic charge.

In the following year Rutherford obtained, with Royds, complete spectroscopic proof of the identity of the α particle with helium. A point to be noticed here is the concentration of Rutherford's interest at this stage on the properties of the α particles. The work at McGill had fully established the validity of the disintegration theory, and the sequences of changes in the active deposits of radium, thorium and actinium had been fairly completely elucidated, so Rutherford's main interests naturally turned to the properties of the radiations, and in particular to those of α particles. His interest in the radioactive families was revived later by the discovery in his laboratory of short-lived members of the actinium and thorium series, and of the branching which was found to occur in all the three main series, but it was on the radiations that he did most of his work after 1907. There is a deep significance in the changes of title in his books—from *Radioactivity* in 1904 and 1905 to *Radioactive Substances and their Radiations* in 1912 and the *Radiations from Radioactive Substances* of Rutherford, Chadwick and Ellis in 1930.

Other work on, or nearly related to, the properties of the α particles in which Rutherford took an active and personal part during the pre-war period in Manchester included the accurate measurement (with Robinson) of the specific charge

and velocities of the particles, and of the variation with time of the heating effect of the active deposit of radium. At the same time, a great deal of important work was going on under his general direction; of this, we need only mention Geiger and Nuttall's measurements of the ranges of the particles from different elements, which were summarized in the well-known Geiger-Nuttall relation between range and transformation constant. The work which had the most profound influence on the later development of the subject—that on the scattering of the α particles—was begun by Geiger in 1908 and continued in association with Marsden from 1909 onwards. Further reference to this will be deferred for the moment.

Rutherford also had many people in the laboratory at work on β -ray problems, and one of Moseley's first researches was a determination of the number of particles emitted in β disintegrations. Rutherford himself did not take a particularly active part in β -ray work until after he had put forward the nuclear theory of the atom. He then recognized the possibility of obtaining information on atomic structure from a study of the β rays, and with Robinson he investigated in 1913 the β -ray spectra of radium B and C. Later, with Robinson and Rawlinson, he began a similar investigation of secondary β -ray spectra, but this was interrupted in 1914.

About the same time, and for similar reasons, he developed a stronger interest in the γ radiations. Much important and intricate work had already been done in the laboratory by Gray, Florance and others, and Rutherford had himself collaborated with Chadwick in a γ -ray research. About 1912 he began a large-scale attack upon the difficult problem of analysing the γ radiations from a number of radioactive bodies, at first, with Richardson and others, by absorption methods. In 1913, with Andrade, who had just come to Manchester as John Harling Fellow in the University, he measured a number of γ -ray wave-lengths by the newly discovered method of reflection from crystal faces. The transmission method of using the crystal was invented in the course of this work.

Rutherford's greatest single contribution to physical science was based on an apparently minor detail which emerged from the α -particle scattering experiments of Geiger and Marsden. It had been found by these workers that when a pencil of α particles passed through a thin metal foil—a foil so thin that the average angle of scattering was no more than a degree or two—a quite unexpectedly large fraction of the particles (roughly one in 10,000) experienced deflections of more than a right angle. Rutherford's brilliant solution of the problems raised by this observation—his nuclear theory of atomic structure—was published in 1911 (*Phil. Mag.* **21**, 669). In this paper he worked out fully the laws of single scattering of α particles by a nuclear atom, and his deductions were quantitatively verified in further experiments by Geiger and Marsden.

The next two significant advances in nuclear theory had their origins under the direct influence of Rutherford. In 1913 Bohr showed that if certain quantum principles were applied in the description of the motions of the extranuclear electrons, Rutherford's atom-model could be made to lead to a quantitative explanation of known regularities in optical line-spectra. In the same year Moseley, in an equally brilliant experimental research, was able to show how X-ray spectra

depended upon nuclear charge, and to establish the importance and precise significance of the concept of *atomic number*. Bohr's three papers on "the constitution of atoms and molecules" and Moseley's first paper on "the high-frequency spectra of the elements" were all communicated by Rutherford to the *Philosophical Magazine*, and they appeared respectively in the numbers of that journal for July, August, September and December, 1913.

Before the lines of research opened up by these new discoveries could be at all fully exploited, war was declared, and Rutherford's research school was almost completely broken up. He carried on research with the remnants of his school, but more and more of his time was taken for official war work, and though he had in Evans an exceptionally good and capable senior lecturer, it was difficult to carry on the routine work of the Department with a staff so heavily depleted. Most men would have found it impossible to do creative work under these conditions, and it is characteristic of Rutherford's energy and enthusiasm that he should have emerged, only a few weeks after the Armistice, with an experimental research of the very highest importance. This was the work, published in the *Philosophical Magazine* for June, 1919, in which he showed from beautiful experiments, strictly controlled, that the nitrogen nucleus could be artificially disintegrated by the impact of fast α particles, and that a fast proton was one of the products of the disintegration. At this time there were practically no research students in the laboratory, and Rutherford enlisted his laboratory steward, Kay, to help in counting scintillations. This was the last work he published before he left for Cambridge, and it was the starting point of a whole series of brilliant investigations.

It is now time to say something of the laboratory which, as we have seen, saw the birth of the nuclear atom and the first experiments on artificial disintegration of the elements. The Manchester University Physical Laboratory had been designed with great care by Rutherford's immediate predecessor, Arthur Schuster, who was a very fine physicist and something of a pioneer in organized physical laboratory instruction. The laboratories were nearly new (they had been opened in 1900) and they were well equipped for electrical work. Further, there was a good electrical engineering department, which a few years later became an independent department under the control of Professor R. Beattie, but which was in 1907 at least nominally a part of the department of physics, and was housed in the same building. This arrangement was of immense advantage to the physics department, as it made it possible to have instruments for research quickly and accurately calibrated, and Beattie and his staff were always most helpful with advice on problems of electrical measurement and equipment.

The laboratory also had a liquid-air machine and—perhaps even rarer at that time, and certainly more important—a laboratory steward, William Kay, who could be relied upon to make it work whenever liquid air was required. Rutherford therefore came to laboratories which were very suitable for research in radioactivity. He brought some radium with him, and later the Austrian Government, recognizing the importance of his work, lent him a larger supply—about 450 milligrammes of radium bromide—with which much of his Manchester work was done. Geiger,

who was already in Manchester—he had started work there with Schuster—was immediately taken into working partnership, and soon became Rutherford's right-hand man, and unofficially a sort of assistant director of radioactive research.

Rutherford was not overburdened with administrative or teaching duties, and he was helped when he came to Manchester by a young and enthusiastic assistant staff, with whom he was immediately on the best of terms. Most of the members of his staff took part in radioactive research, and W. Makower (Senior Lecturer, and later Assistant Director of the Laboratories) collaborated with Geiger in a textbook on experimental radioactivity which was based on the course of instruction developed in the Manchester laboratory. Rutherford was also fortunate in his colleagues outside the physics department. In particular, he found in Horace Lamb, the distinguished head of the mathematical department, a very good friend and a wise counsellor in matters of University politics.

Rutherford then slipped easily and comfortably into life and work in Manchester. Manchester liked him at sight, and he gave every appearance of liking Manchester. This certainly meant that he did like Manchester, for he was never very gifted (or even assiduous) in concealing his dislikes.

His post at McGill had been a research professorship, and I imagine that he had done little formal lecturing to degree students before he came to Manchester. In my time as a student, he lectured only to the elementary (Intermediate) class and on electromagnetism to the second-year honours class. Technically, I suppose that he was not a very good lecturer—that is, he had none of the arts of the trained orator, and he sometimes got his sentences oddly twisted up when he embarked too eagerly on the explanation of something that interested him very much—but he was the most inspiring lecturer I have ever heard, and he was blessed with a naturally good and pleasing voice. Although it was no part of their official course, the honours students used always to attend his Intermediate lectures. This was no doubt partly because the lectures were good fun—Kay loved to devise and set up elaborate and beautiful experiments, and Rutherford loved to show them; it was in fact sometimes said that the lecture course was largely dictated by Kay—that Kay set out the experiments he thought appropriate to the time of year, and Rutherford came in, looked round the lecture bench, and lectured on whatever he found there. The real appeal of Rutherford's lectures to the better students was, however, due to his extraordinary gift of seeing the essential *physics* in any problem, and imparting it to his hearers; even if a man already knew a good deal about the subject matter of one of Rutherford's lectures, he was bound to get a new, and sometimes dazzling, light upon some aspect of it after it had passed through Rutherford's mind. In later years this gift was made apparent to much wider audiences, and it is probably very generally known to-day; I stress it specially here because it was an important factor in Rutherford's outstanding success as a teacher in Manchester. His more advanced lectures, and especially his lectures on his own subject, were a pure delight. Moreover, it should be noted that Rutherford took teaching as a serious responsibility—in spite of his own devotion to research, he had no patience with the

type which affects to regard the efficient teaching of students as an inferior, or even degrading and time-wasting, function of a University teacher.

It was, however, in the research laboratories that his influence was most apparent. He soon filled—and over-filled—them with workers from all over the world, leavened as time went on with a good proportion of students of his own training. He continued, with no apparent effort, to find space, apparatus and ideas for research for this large team, and yet to do a great deal of experimental work with his own hands. The problem of finding space was simplified a few years later, by the provision of additional accommodation, but the apparatus problem must always have been fairly serious, as it is unlikely that his departmental grant could ever have kept pace with so rapidly expanding a volume of experimental work. That this problem was solved at all, can only be attributed to Rutherford's genius for devising simple and effective experimental methods. The magnitude of the laboratory's output of experimental research was not so much due to the possession of large financial and technical resources, as to Rutherford's amazing fertility in ideas for new experiments. In a large proportion of the ionization measurements made in the earlier years in Manchester, the only electroscopes used were made from discarded cigarette tins. A Fleuss pump had to serve many masters, and was dragged from room to room as required; in my first work with Rutherford on β -ray spectra, we used to evacuate the whole apparatus from scratch with a hand-operated Toepler pump—and I remember that Rutherford taught me to use the pump in the dark, judging the stage in the cycle of pumping operations by the "feel" of the mercury reservoir in the hands.

In assessing the magnitude of Rutherford's personal contribution to science during this period, it should be kept in mind that he was extraordinarily generous as a collaborator in, and director of, research. If his name appeared on a joint paper, it meant that he had taken a large personal share in the experimental work, and many papers on which his name did not appear were full of ideas which he had freely given. He spent a great deal of time in going round the laboratories and discussing with each research worker his results and difficulties. The magnitude of the published work which bears his name, impressive though that is, falls far short of his *effective* output.

His genius as an experimenter and his skill with apparatus were fully appreciated by his school in Manchester. It was strongly held in the laboratory that he could take liberties with apparatus which would inevitably have been disastrous if attempted by lesser men. It is certainly true that he practically never broke anything; it was at times almost exasperating after one had been struggling, for instance, for ten minutes to coax along a mercury pellet that was blocking some narrow section of an elaborate and fragile system of glass tubing, to see Rutherford come breezily in, hit a tube really hard at exactly the right point, and send the mercury scuttling obediently to its appointed place. Yet, in spite of his own skill, he was wonderfully tolerant of the effects of clumsiness in others, unless he suspected that there had been real carelessness. He found it difficult to forgive anyone who admitted mercury to the barrel of a Fleuss pump.

After this, I cannot resist the temptation to tell the story, with its very characteristic sequel, of an isolated instance in which Rutherford's hand showed less than its usual cunning. There was a rather elaborate pumping train that was used for collecting and purifying radon, and one day I found a connecting tube cracked right across at a point very close to a stopcock. This tube joined two quite heavy pieces of apparatus, each standing in its own mercury tray; the glass was probably rotten through prolonged exposure to radon, and the nearness of the crack to the stopcock made an effective repair almost impossible. An experienced glassblower would have condemned the section at once, but as I knew too little to realize all the difficulties, I tried to join the two broken ends. As it happened, I had beginner's luck; I got the joint almost completed, and, with the glass nicely flowing, I was just adding the finishing touches with a spicule of patching glass when Rutherford came in. This, of course, was a sight he could not resist, "Ha!" he said, "you want them closer together", and he pushed one of the trays towards the other. Unfortunately, the apparatus being heavy and the floor not very smooth, the tray came in a good two inches once it had begun to move, and the joint was ruined beyond redemption.

Rutherford at once realized the extent of the calamity, and exerted himself to cheer me—"I'm terribly sorry; I know how annoying it is—of course I used to do a *lot* of glass-blowing myself when I was younger." No doubt I visibly pricked up my ears at this, and Rutherford, pleased with his effect, went on: "I used to make X-ray tubes—lots of 'em!"—then, realizing that he'd been carried too far, he hastily added, with a characteristic twinkle: "Only little ones, of course!"

Rutherford's phenomenal memory was another source of pride, and sometimes of amusement, to his Department. He appeared to have a sort of mental card-index of all the more useful measuring instruments in the laboratory—certainly of all the good ammeters and voltmeters—and I think that when Beattie took the Electrical Engineering Department over into new quarters he had some difficulty in getting away with his own materials. But Rutherford not only remembered permanent apparatus—he seemed to remember every tube that had been filled with radon. If somebody wanted a supply of radium D-E-F, and the old radon tubes were being collected, he would say, "What about that 100 millicuries that Makower and Moseley had?"—referring to some source which had been given out perhaps two years earlier. His research assistant knew that even if he did not immediately report the accidental destruction or loss of a radon tube, there was no chance of its remaining undiscovered for long.

Rutherford was, of course, first and always an experimenter, and an experimenter with an uncanny knack of knowing just what experiment ought to be tried, and how to set about it. It has often enough been said that he was no mathematician, but this has most often been said by men with far less real mathematical sense than he had. It is obvious that his mathematical attainments were less, for instance, than those of his predecessors in the Cavendish chair, but as Professor Eve has recently pointed out, if he really needed a piece of mathematics he could generally produce it. Eve made this remark in connexion with Rutherford's first

handling of the equations of radioactive transformation, and I can recall other instances. When, for example, we were measuring the ratio E/M of the α particle, we took photographs of the electrostatic and magnetic deflections of the three groups (radon, radium A and C) of particles from a radon source contained in a glass α -ray tube. We measured the plates one afternoon, and made a hasty calculation of the results. Even a rough calculation sufficed to show clearly that the three groups gave markedly different values for the specific charge, and there was no obvious explanation. We went home in rather chastened mood to think it over, and Rutherford arrived early next morning with a complete and elegant solution, which he had obtained overnight. It was not a very simple problem, but he had succeeded in showing that the explanation lay in the retardations experienced by the particles in traversing the walls of the α -ray tube. Particles of a given velocity were less retarded if they passed through nearly normally than if they passed through obliquely, and the resulting differences in velocity on emergence gave rise to a displacement on the photographic plate of the centre of gravity of the deflected pencil. Rutherford had worked out the full theory of this effect, and when we re-measured the plates in the light of his calculations, measuring to the edges and not to the centres of the displaced lines, we found agreement to within 1 part in 1000, in place of discrepancies of over 1 per cent. Again, the semicircular focusing method which we used for β -ray spectra was not essentially new, but I think that Rutherford was the first to see clearly the underlying principle, and to exploit it fully. Mathematician or no mathematician, he had a very sound geometrical instinct, and with a little trouble I think he could have beaten many professed mathematicians at their own game.

In the Manchester laboratory, any really heavy mathematical work could be handled by the Reader in Mathematical Physics. The readers in Rutherford's time were Bateman, Darwin and Bohr, all of whom made contributions to radioactive theory. Darwin and Bohr made notable contributions to the theory of the passage of α and β particles through matter, and Bateman put the transformation equations into a more symmetrical form. The readership, instituted through the generosity and foresight of Schuster, was a most valuable addition to the all-round strength of the Department—and I think the readers would readily admit that for their part they gained a great deal by being brought into contact with Rutherford and the problems which his work provided. Darwin, indeed, was so moved by the spirit of the place that he began experimental research in radioactivity. Later he became interested in X rays, and besides making a classical contribution to the theory of X-ray reflection he did experimental research with Moseley and independently.

Rutherford's personal relations with his colleagues and students were of the happiest. Much may often be learned from a man's nickname, and Rutherford's in Manchester ("Papa") was a mark of sincere affection.

He ruled in the laboratory as a benevolent despot, and he knew exactly how to get the best amount of work out of every member of his sometimes oddly assorted team of research workers. The main reason for his success in this was that he was

leading his team rather than driving it. Perhaps he did drive it a little—it would be idle to deny that there was sometimes a slight, but conscious, slackening of effort on those Thursdays when he was known to be reading a paper to the Royal Society—but he did not over-drive. He did not bully, and it was not in him to nag. People who worked hard for him did so largely because he was so obviously eager to know the results of their work; even if a man had no great inward stimulus to the work on which he was engaged, he was sure to be caught by something of Rutherford's enthusiasm. Sometimes the excited activity was of short duration, but often it endured.

Rutherford's attitude to long hours in the laboratory was charmingly inconsistent. Officially he was opposed to late night work—but he had a habit of leaving the laboratory about seven, and on his arrival next morning at nine asking how the work had gone in the meantime. Further, it was not unknown for him to look in quite late—perhaps while driving back with Lady Rutherford from the theatre—to see how things were going on. But he was very quick in applying the stopper if he thought anyone was beginning to show signs of overwork.

His interest in his students and their well-being was not confined to the laboratory. He and Lady Rutherford entertained a great deal, and at their house in Withington the research students made a number of outside contacts, with members of other University departments, with guests from outside, and with visitors from abroad. This was all to the good, as the research school was a large and happy family, and it might well have tended to become too self-contained and self-centred a unit. There was a lot of interesting gossip at the Sunday evening gatherings in the Rutherfords' house, and it was part of a liberal education to hear, for instance, Rutherford and Lamb together in reminiscent mood. Lamb's interests had always been largely in the more physical side of his subject; he was much the older man, and his recollections went back to the time of Maxwell. Lamb was less easily than Rutherford lured into verbal indiscretion, but he had a strong sense of humour and a very shrewd judgment, and in his company Rutherford was always at his best and most entertaining. "Shop" was not, of course, by any means the sole topic of conversation, but a great deal of informal knowledge of physics—and physicists—was to be picked up on such occasions as this.

Rutherford had a genius for easy friendship with young and old alike. His immense vitality and unaffected, buoyant good-nature won him friends everywhere, and he made a wide, deep and lasting impression in Manchester. As one of the oldest and reputedly the most crabbed of the University officials said to me just after he had left for Cambridge: "Your Chief was like a breath of fresh air about the place." At any meeting of any of his old students or colleagues almost the first words were sure to be "Seen or heard anything of Rutherford lately?"—and so long as any of us survive, his memory will always be green.

§ 5. THE CAVENDISH CHAIR

By Prof. C. D. ELLIS, F.R.S.

Rutherford came to Cambridge in 1919, and to-day the Cavendish Laboratory represents his work done in the intervening years. The Laboratory was his greatest experiment, and like the apparatus in an experiment it grew organically with but little planning. Had he lived we should have seen the results of this great experiment put into permanent form, and no one who knew Rutherford can doubt that it would have carried the stamp of his personality. But the experimenter is dead and the experiment is to be completed by others. It is the fate of all great men to leave unfinished work, and not the least of the tragedies associated with Rutherford's death is that he could not have been spared to rebuild his laboratory and fit it for many years to come to carry on his traditions.

Rutherford's work at Cambridge is well known and a full description would mean recounting the development of nuclear physics in the last two decades. This is not the occasion to attempt that task, and just a few recollections of his personal experiments seem most fitting. Soon after he came to Cambridge he found the time to follow up vigorously the experiments on the artificial disintegration of the light elements which he had started during the war period. In those days the experiments still involved only simple apparatus and were of the type Rutherford loved. A radioactive source provided the α particles which fell on a foil of the material to be disintegrated, and the resulting protons, hitting a zinc sulphide screen, were detected by the scintillation method. The whole apparatus was contained in a small brass box and the scintillations were viewed with a microscope. I can well remember being surprised, in fact mildly shocked, that the apparatus was not more impressive, yet these experiments, so simple on the surface, required the highest experimental skill to make them yield dependable results.

Counting the scintillations was difficult and tiring, and Rutherford usually had one or two of his research students to help him. The experiments started at about four in the afternoon and we went into his laboratory to spend a preliminary half an hour in the dark to get our eyes into the sensitive state necessary for counting. Sitting there, drinking tea, in the dim light of a minute gas jet at the further end of the laboratory, we listened to Rutherford talking of all things under the sun. It was curiously intimate but yet impersonal and all of it coloured by that characteristic of his of considering statements independently of the person who put them forward.

Soon his assistant Crowe would appear with the radioactive source, which had required long and careful preparation, and while the lights were turned up for him to fix it in the apparatus, the counters and Rutherford would either keep their eyes tightly closed or huddle into a little wooden shed built in one corner. Then counting would start, each in turn taking his place at the microscope for a minute. It was very striking how Rutherford could keep entire control of the experiment. Working in comparative darkness, with no time to waste since the radioactive source was

decaying, he would sum up instantly the implications of the results and issue his directions. The secret, I am sure, was that he thought so deeply about the experiments that he had already anticipated the results before he started. All the relevant quantities were calculated in advance and he detected instantly the first indication that something unexpected was happening. He was the complete antithesis of the man who observes first and then goes home to work up the measurements to find out what has happened. As the scintillations were recorded Rutherford compared them with what he expected and translated them at once into the final deductions from the experiment. Sometimes, only too frequently, the dreaded contamination would occur. Despite all precautions some of the radioactive material would become detached from the source and reach a part of the apparatus from where the primary α particles could reach the scintillation screen. In no uncertain way Rutherford would express his feelings, there was no question of detached philosophic calm, his attitude to the experiments was far too human and personal for that.

As time went on the experiments became more and more laborious and progress slower, and despite the brilliant results obtained by Rutherford and Chadwick by these methods it was clear that the limit was being reached. He therefore initiated investigations on the possibility of using electrical methods of counting. Eventually, owing to the able work of Wynn-Williams, these were brought to an efficient and dependable state and he returned once more to his beloved α particles. He saw that these new methods were capable of supplying far more detail than had been obtainable by the older technique, and both by his own experiments and by those of others in his laboratory he led a new investigation of the nuclear structure of the heavy radioactive elements. It was towards the end of this period that there came the discovery of the disintegration of the light elements by protons, of the neutron, and of induced radioactivity. Rutherford's personal experiments, now in collaboration with Oliphant, were on the disintegration of the light elements by protons and deuterons by means of relatively slow particles, whose poor efficiency was offset by the intensity of the beam. This is all recent history and his work in this field is well known. Had he lived he would have turned his attention to the use of the fast particles produced in the new high-voltage laboratory he had planned and developed.

Rutherford had a genius for working in the right direction. Any competent experimenter could have done most of his work, but anyone except Rutherford would have strayed from the path. The extent of his advances is due primarily to the fact that he went forward in a straight line, and had that deep insight which told him when a reasonable experiment was only really a side line; when a certain measurement, though important, could yet afford to be left a while; and when, although good experiments were waiting, they were not really progressive and it was the moment to abandon old methods and develop new technique. While he was always striving to develop technique, I believe that he regretted the passing of the old simple and direct experiments, and as the apparatus became more and more complicated, so the experiments became less personal, and the final results became more remote and only obtainable after analysis when the experiments had long been finished. He loved lecture demonstrations, when, despite the complica-

tion of the apparatus, he could produce instant and visible effects of the fundamental phenomenon.

Perhaps the most characteristic example of his genius during his Cambridge period is to be found in a paper, *Phil. Mag.* 4, 580 (1927), which at the time made little impression and is now almost forgotten. It puts forward a theory about the origin of the α particles, and the details of this type of disintegration, which was soon completely superseded by the wave-mechanical picture. Yet what is so interesting is that it shows how completely he had appreciated the difficulties that lay in the way of any explanation on classical lines. From his own experiments on the scattering of α particles and from those carried out in collaboration with Chadwick, he became convinced that the inverse-square electric field round a heavy nucleus must be valid to such small distances that the potential energy of a nucleus and α particle could reach values of ten million electron-volts. Even if an α particle, by some mechanism, just trickled away from the attraction of the main nucleus, it would find itself in this strong repulsive field, and could not possibly emerge from the atom with kinetic energy less than ten million volts. Yet the α particles from uranium have energies of less than six million electron-volts. The hypothesis he suggested to overcome this difficulty is to-day unimportant, but the fact on which he based his argument is recognized to be one of the crucial points which show the need for some theory other than classical mechanics in dealing with these matters. Rutherford's ability to seize on one definite fact, to realize that independently of all other arguments it showed a fundamental error in the current physical picture, and then to follow this trail wherever it led, this ability was the measure of his genius. It is shown no less strikingly in this example than in his famous deduction from the fact that α particles could very occasionally be scattered through large angles. In the latter case he found the right answer, in the former he did not, but the real achievement was the realization of the experimental fact and insistence on its importance.

It is impossible to describe the work of all the people who worked in his laboratory. The majority of the experiments were really started by his direct or indirect suggestion, although he was always willing to let anyone go his own way, and in fact invariably asked for suggestions both from the permanent members of the laboratory and from newcomers. Even in the later years when he had so many outside responsibilities he took a deep and personal interest in all the researches and stimulated all stages of the work to a remarkable degree. His grasp of the implications and true interest of the experiments was extraordinary, but it was by no means always immediately apparent. He would come round to see what was happening and frequently the conversation became positively awkward because he would talk so vaguely and confuse all the relevant terms to such a degree that it was difficult to avoid correcting him, a step not lightly to be undertaken. He would leave and one would reflect on what a remarkably clear grasp one had of the problem. In fact so clearly did one see what was the next step to take and what lay beyond, that really the only thing to do was to see Rutherford and tell him about it properly. Then as one arranged one's thoughts would slowly come the conviction that this

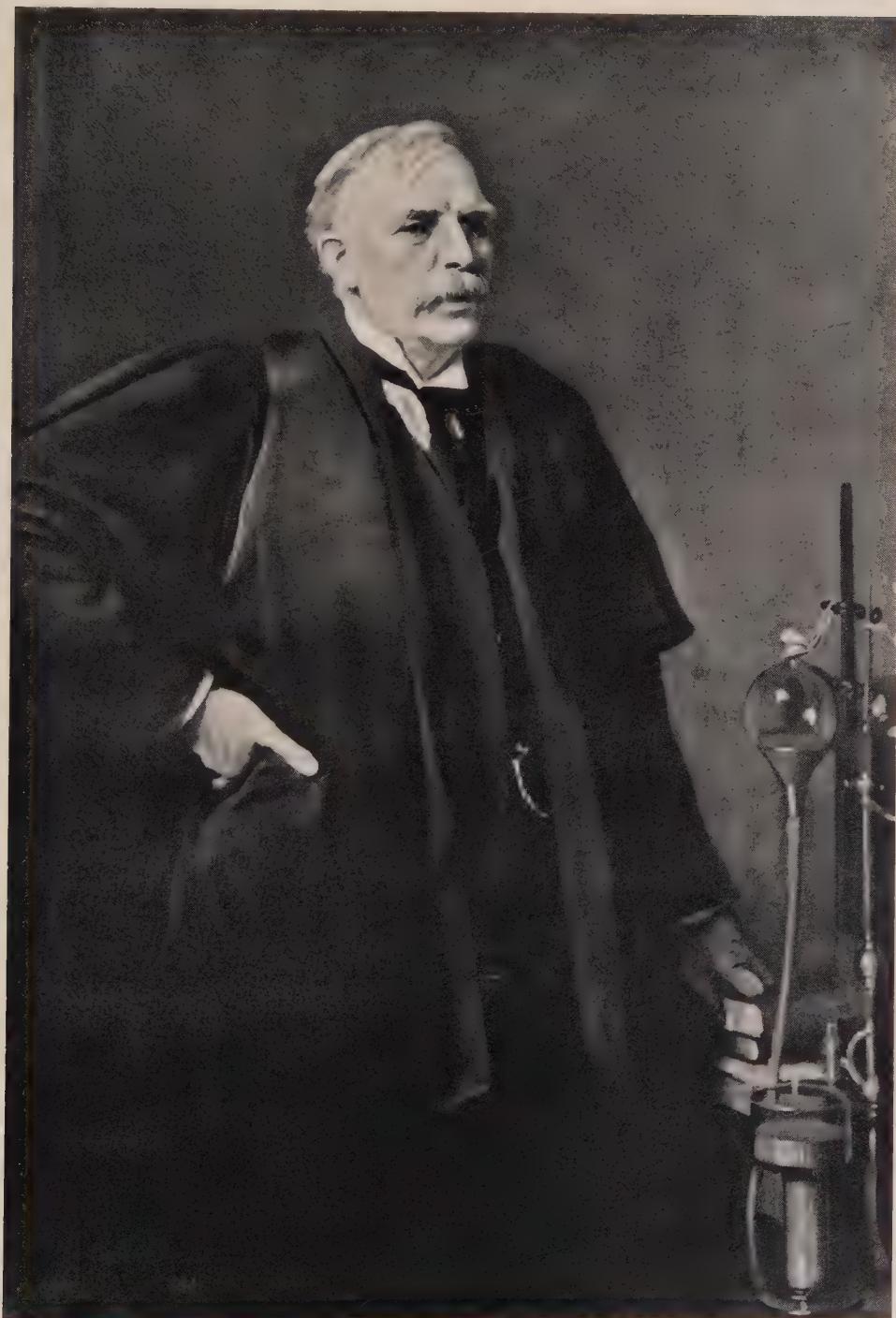
was just what he had been saying, that he had seen it all far more precisely and that this wonderful new idea was only the slow working of his inspiration. He had such a simple outlook, so unbiased by current theoretical ideas, that it was difficult to appreciate immediately all that he meant just because it was so direct and so simple. He did not think logically, it would be far more just to say that he had an artistic feeling of the way nature works. It was always so clear to him what was the next thing to do that he neither would give reasons for it nor felt the need to do so, he did not in fact appear to be greatly interested in what current theory might have to say for or against his ideas. To the end he was unappreciative of quantum mechanics, and had little use for the wave picture. Particles were particles and that was the end of it.

At the beginning of every Michaelmas term he would speak at the first meeting of the Cavendish Society and give a review of those advances of the past year in which he had been particularly interested. He obviously enjoyed this occasion when, to use his own phrase, he told the boys all about it, and his enthusiasm and conviction of the importance of the work were clear to every one. He was a natural leader, not because he particularly wanted to dominate but because he was completely sure that he was doing the right thing and intended to go on doing it. Other people who followed him were obviously sensible; if they did not follow him, he did not attempt to force them but he had the gravest doubts about their wisdom.

Rutherford bore his share of university and college administrative duties, and served on many important committees. I think he did not like the committee method of administration and found the work rather tiresome. He never really appreciated the essential democracy of Cambridge, although he of all men was, in some senses, the most democratic. He was just as likely to tell some important and distinguished person what an unimportant person had said as vice versa, in fact these distinctions did not exist for him. Yet anything that impeded the fulfilment of what was to him the obvious thing made him impatient, and it was an interesting example of restraint to hear him putting forward a persuasive argument at a board in favour of a project when he had already made up his mind that it was going to be realized.

He used to dine at Trinity on most Sundays, and fairly frequently once or twice during the week. He had not much use for fine wines and frankly confessed his lack of appreciation. What he wanted after dinner was a pipe and rarely did he go to the Combination Room on ordinary nights. In the smoking room, by the force of his joviality and humanity, he usually gathered round him a group of people who would be discussing anything except physics. He was at his best when discussing incidents from his early days. Interested in people, and with a tenacious memory, he would recount events and conversations in such a vivid manner that he could hold the interest of any group of people.

Towards the end of his time at Cambridge he was increasingly occupied with outside responsibilities, but yet he kept absolute control of his laboratory. In that large rambling collection of buildings his personality was everywhere. It is still the Cavendish Laboratory but it is no longer Rutherford's Laboratory.



Photograph of the portrait painted by Oswald Birley

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**SIR HERBERT JACKSON, K.B.E., F.R.S., Emeritus Professor
of Chemistry in the University of London****1863-1936**

SIR HERBERT JACKSON died, after a short and painless illness, at Parsifal Road, Hampstead, on 10 December 1936, in his 74th year. He was born on 17 March 1863 on the Surrey side of London and came of a family which had its origins, or some of them, in Yorkshire. However, he lived nearly all of the earlier and most of the later part of his life in Hampstead. He was educated at King's College School until he entered King's College, where he worked as student, Daniell Scholar and Student Demonstrator under Professor C. L. Bloxam, much of his work being done in Professor Bloxam's private laboratory. He was appointed Lecturer in Chemistry soon after John Millar Thomson had succeeded Bloxam as Daniell Professor in 1879, became Assistant Professor in 1902 and Professor of Organic Chemistry in 1905. He was elected a Fellow of King's College in 1907 and appointed Daniell Professor of Chemistry in succession to Thomson in 1914. He resigned this position in 1918, with the title of Emeritus Professor of Chemistry in the University of London, on his appointment as Director of Research of the British Scientific Instrument Research Association, a position which he held until 1933, afterwards acting as consultant to the Association and as a member of its Research Committee.

As a young man Jackson was a good all-round athlete with notable or creditable achievements in such varied directions as running, Rugby football (in this field he was regarded as a possible England cap), step-dancing and boxing, among others. Throughout the period (nearly 40 years) during which he was associated with King's College he took part in the annual sports either as competitor, as judge, or in some other capacity on almost every occasion. However, the writer is compelled to add that he took a share or an interest in almost every activity, of whatever kind, of any importance which was connected with the College.

A great difficulty in writing an account of Jackson's scientific work arises from the paucity of his publications. These are few and quite inadequate and out of proportion to the immense output of experimental investigation he accomplished. A very fluent talker and an excellent and facile experimenter, he seems to have found writing either burdensome or distasteful. In 1883-4 he contributed three notes to the Chemical Society on "The action of sulphuric acid upon potassium iodide", "Bromine as a test for strychnine" and "The action of arsenious anhydride on glycerol".

In or about 1890 Jackson began a remarkable and extensive series of investigations on phosphorescence. These included the production of fluorescent and phosphorescent materials, their behaviour when excited by ultra-violet light and by exposure to electric discharges in low and high vacuum discharge tubes, and the effect of the form of the glass envelope and of the shape and position of the electrodes on the resulting phosphorescence. During these experiments he discovered that in a high-vacuum discharge from a concave cathode of uniform curvature the excitation

of the phosphorescent material used as anticathode could be confined to a small area about the centre of curvature of the cathode. In some cases the phosphorescent substance became appreciably heated over this area. It will be recalled that similar observations had been made upon other materials by Crookes in 1874 to 1879. Some of Jackson's tubes had anticathodes made of various non-phosphorescent substances, including metals, to find out whether such materials emitted invisible phosphorescent radiations when excited in an electric discharge tube. Jackson made all his own tubes and did all his own glass work. The amount and quality of such work required for success in these researches are such that they form a striking testimony to his industry and enthusiasm, as well as to his manipulative and experimental skill. In the course of this work he experimented in almost every conceivable way, with spherical and pear-shaped tubes and tubes with necks (something like a sealed-off flask) and tubes with electrodes of different shapes and in various positions. One thing that rather puzzled him was this. He found that some concentration of the phosphorescent response could be obtained with convex cathodes if they were mounted so as to intrude a short distance into the necks of necked tubes, the degree of concentration depending on the degree of vacuum. This focusing effect is probably due to electric charges developing on the walls of the neck near the convex cathode. With the convex cathodes mounted so as to project well beyond the opening of the neck and so as to reach nearly to the centre of the spherical part of the envelope a distribution of phosphorescence fairly uniform over the spherical glass wall was obtained.

Much to his regret the writer never discussed with Jackson the further interesting developments of these researches. As there are some matters of considerable historical importance involved he will take the liberty of quoting the words of one who has often discussed them with Jackson and is therefore in a position to express an authoritative opinion. In an account appearing in the *Obituary Notices of Fellows of the Royal Society* (January 1938) Dr H. Moore writes: "To detect any ultra-violet radiation which, originating at the cathode, might be transmitted through the glass walls of the tube, he used screens of phosphorescent materials held close to the tube and in some cases observed that the screens glowed visibly.

"His interest throughout this work was in the phosphorescent effects rather than in the mechanism by which they were produced. His views regarding that mechanism, stated many years later in conversation, were that the electric discharge caused the cathode to emit ultra-violet radiation which, falling on the anticathode, excited the phosphorescent response on the anticathode material. The glow of phosphorescent material held outside the tube was considered to be a secondary phosphorescence excited by ultra-violet radiations present in the primary phosphorescent emission from the anticathode. The fact that radiations emitted by the anticathode could penetrate the glass walls of the tube, and could excite a screen held outside the tube, was taken to indicate that the wave-length of the radiation emitted by the anticathode was not shorter than 3000 Å.

"There can be no doubt that the response of the phosphorescent screens held close to the tube was, in some cases at any rate, due to X rays emitted by the

anticathode and that, had the observations been viewed from a different standpoint, Röntgen's discovery might have been considerably anticipated. At no time, however, did Sir Herbert Jackson advance any claim to be the original discoverer of X rays, or countenance any suggestion that such a claim might be made on his behalf. Throughout these investigations he had considered that he was dealing with comparatively long-wave ultra-violet radiations and he expressly stated on several occasions that the characteristic penetrating power of the radiations emitted by the anticathode was neither discovered nor suspected by him."

In a paper read on 5 March 1896⁽¹⁾ Jackson described a discharge tube, fitted with a concave aluminium cathode and an inclined platinum anode, which he had made and used during January 1894, and with which, or with a replica of which, he had been able to reproduce all the effects described in Röntgen's original announcement in December 1895. This tube, the original Jackson "focus-tube", was used in May 1896 for a demonstration of X rays at a *Conversazione* held by the Royal Society. A very characteristic action at this demonstration was that at one stage Jackson held up his shoe and showed the onlookers the metal nails in the soles projected on the phosphorescent screen. The main features of this tube were adopted universally for the construction of all gas X-ray tubes.

Jackson gave a discourse on phosphorescence at the meeting of the British Association at Bristol in 1898, and a series of juvenile lectures on it at the Royal Society of Arts in 1900. A published account of some of his work on phosphorescence is to be found in *Nature*, vol. 58, p. 559, and the B.A. Reports for the Bristol Meeting, 1898. The account in *Nature* contains many interesting and important statements; among them, that he had prepared specimens of lime which could not be distinguished from pure lime by chemical analysis, but gave rise to red, orange-red, orange, green and blue phosphorescence respectively.

Between about 1900 and 1914 Jackson devoted himself mainly to problems in pure and applied chemistry. Most of this work is unpublished. What is known about it may be found by consulting the notice by H. Moore in the *Obituary Notices of Fellows of the Royal Society* and another, by Richard B. Pilcher, in *The Analyst* for February 1937.

Among his more miscellaneous activities between 1890 and 1914 are the following. He undertook an elaborate investigation of the weathering of stones in Canterbury Cathedral, Westminster Abbey and other buildings, and did a considerable amount of experimenting on methods of treating stones so as to avoid or diminish damage to stones by weathering. He also became interested in the scientific problems presented by laundry work and investigated the action of alkalis, chemical solvents, oils and soaps on different materials and also their detergent action for cleaning materials soiled in various ways. As a result of the information thus obtained he arranged a course of lectures and practical work on the subject at King's College. This was well attended by launderers from a large area, and the practical value of the work and of the advice which Jackson gave in answer to questions raised by those attending the course were much appreciated. In fact, the importance of the step he took when he put his chemical and physical

knowledge at the service of the laundry industry in this very effective manner has been increasingly recognized by those engaged in it. An account of his work on detergents and bleaching agents was given in two series of Cantor Lectures to the Royal Society of Arts in 1907.

Before this he had been investigating the growth of plants in atmospheres free from carbon dioxide but containing various proportions, from 1 to 70 per cent, of carbon monoxide. He found that green plants could grow in such atmospheres and that starch was formed in them during their growth. This work was continued later, in collaboration with Professor Bottomley⁽²⁾.

In 1906 we find him working, in collaboration with D. Northall-Laurie, on the behaviour of acetylene and of vapours of methyl alcohol and acetaldehyde with electric discharges of high frequency. Accounts of these were published by the Chemical Society. In 1906 also he gave a course of juvenile lectures on combustion and flame at the Royal Society of Arts.

Among the very numerous subjects which he studied and experimented on were methods of promoting crystallization of solids by heating in the presence of various salts, the dispersion of clays in colloidal suspension, the production and testing of refractories, chemical reactions between solids at high temperatures, physical changes in solids at high temperatures, pottery and porcelain, glasses, and problems arising in the manufacture of gun-cotton. As a result of his work on this last subject he made suggestions for modifications in the processes of manufacture with the object of retarding such deterioration of the product as might lead to its spontaneous combustion when in store.

One striking characteristic of Jackson was his interest in and affection for any instrument or apparatus which was useful for chemical researches or chemistry in any sense. In this category we may perhaps classify his interest in photography. Before dry-plate photography was developed he was experimenting on the preparation and sensitizing of emulsions and on methods of developing plates coated with the different experimental emulsions thus obtained. Afterwards he investigated the suitability of many reducing agents for use as photographic developers, and produced special developers both for ordinary plates and for plates for colour photography. He also developed a variety of novel toning baths for photographic prints. Jackson was a keen and accomplished amateur photographer and had a fine collection of stereoscopic photographs, colour photographs, prints and lantern slides which he had made. On the scientific side he experimented in almost every chemical process involved in photographic technique.

In the use of the microscope Jackson was a master. Familiar with all the usual microscope objects, adept in microscopic manipulation and technique, and having a thorough understanding of the microscope as an instrument, he contrived to make use of it in almost all his work. The numerous purposes to which he applied it included the examination of his chemical preparations and the investigation of the effects of heat and various physical and chemical treatments on clays, fibres, porcelains and other materials, objects and substances. He was intimately acquainted with the appearance of a vast number of subjects when viewed with the microscope

and under different methods of illumination as well as with the diffraction effects presented by various small objects when illuminated in different ways. As a result of this wealth of knowledge and his manipulative skill and dexterity, combined with his insight into chemistry and physics, he was often able to tell more in a few minutes about the nature of a given specimen and what had happened to it than others using the same or different methods could in as many days. He was always ready to put his experience of the microscope at the service of others by way either of advice or of the actual examination of specimens. In fact, it obviously afforded him great pleasure to be allowed to do so in any worthy cause.

Another optical instrument in the use of which Jackson was an expert was the spectroscope. He employed this for the detection of traces of inorganic bodies present as impurities or as colouring agents in drugs, glasses, metals, salts and other substances, or introduced into fabrics, leathers, papers and other materials during manufacture.

At the beginning of the Great War Jackson's advice was sought about a number of problems, including the manufacture of toluene and of certain drugs, and about work connected with the Censor's Office. He also served on many of the committees dealing with the production and supply of essential war materials.

At this period the country was faced with serious difficulties owing to the shortage, and in some cases impending exhaustion, of supplies of a number of special kinds of glass, the majority of which had previously been obtained from abroad and mainly from Germany and Austria. The precise composition and the method of manufacture of most of these glasses were unknown. The task of remedying this situation was entrusted to Jackson shortly after the outbreak of war by the Research Committee of the Institute of Chemistry. This was a matter after Jackson's own heart, and in the prosecution of it he was indefatigable. What he accomplished can only be described as amazing. In a very few months he had developed batch mixtures for about ten kinds of glass, including ordinary soda glasses for laboratory glassware and X-ray tubes, combustion-tube glass, a chemically inactive glass for ampoules, miners'-lamp glass, and other special glasses. The formulae for these were published in the *Journal of the Institute of Chemistry* in April 1915. Sir James Dobbie, at that time President of the Institute of Chemistry, gave Jackson the full credit for these remarkable achievements.

After accomplishing this he worked for the Ministry of Munitions until the end of the war on problems involved in the production and manufacture of glasses and glazes. He developed formulae for a great variety of optical glasses, and also worked out batch mixtures for thermometer glasses, opal backings for thermometers, glasses for artificial eyes, vitrite for the capping of electric lamps, a special heat-resisting glass similar in composition and properties to the Pyrex glass which was produced commercially, though not by him, several years later, and other special glasses. A glass similar to his miners'-lamp glass was immediately adopted for cooking utensils. In March 1916 the President of the Board of Trade expressed the Board's appreciation of the services rendered by Professor Jackson to the glass industry. Much, perhaps most, of this work on glasses was done at night in a small laboratory

which he had fitted up at the top of his house at 49 Lansdowne Road, Holland Park, W. In fact, Jackson worked most of the night as well as all day at this period. The pace would have damaged permanently a man of less robust constitution. It is known from the specimens and records which he kept that the number of experimental melts which he made was considerably over 500, and he developed successful formulae for the production of over 70 kinds of glasses. All through this period he was continually consulted by glass manufacturers and engaged in frequent visits to glassworks all over the country helping to overcome difficulties, which inevitably cropped up in the initial stages of large-scale production. It would be difficult to overestimate the value and importance of his work on the production of glass during this critical period. In recognition of this and of his other war-time services he was created Knight Commander of the Order of the British Empire in 1917. He was also elected a Fellow of the Royal Society in the same year.

In 1918 he accepted the invitation of the Council of the British Scientific Instrument Research Association, created in that year as part of the Research Association Scheme of the Department of Scientific and Industrial Research, to become its first Director of Research. Among the numerous qualities which ensured his success in this capacity were his knowledge of, familiarity with, and affection for a wide range of instruments, his great experimental skill in a variety of directions, possibly unequalled, his insight into what could not be done and what could and with how much and how little difficulty. Other important qualifications were his knowledge of the optical and glass industries and acquaintance with their personnel, his quick mind and rapid grasp of a problem and his sure instinct to get down to the roots of it, his remarkable memory combined with the vast extent and extreme variety of his experimental experience and his thoroughly practical outlook and, possibly the most important single factor, his genial personality. After his retirement from the position of Director of Research of the British Scientific Instrument Research Association in 1933, he was a member of its Research Committee up to the time of his death.

In 1919 he delivered the Sir Henry Trueman-Wood Lecture at the Royal Society of Arts on "Glass and some of its problems",⁽³⁾ and in March 1927 he gave a discourse at the Royal Institution on "Some colouring agents in glasses and glazes".

Jackson was keenly interested in ancient glass and ceramics, particularly Chinese ware. His extensive knowledge of the behaviour of clays and of mixtures of clays and other substances, together with his great skill with the microscope, often enabled him to ascertain the manner in which such objects had been fired and to imitate them. His knowledge of glasses and glazes and of the different colour effects caused by the admixture of different chemicals with glasses of various types enabled him to identify the nature of glazes and the substances used to produce particular colour effects in glasses. In this way he was able to provide archaeologists and connoisseurs with valuable information which up to then had been unknown. One of his striking successes in this field was the discovery of the nature and composition of a scarlet glass of ancient Egyptian origin, which he also successfully reproduced.

Sir Herbert Jackson must have been one of the most versatile men of his time. He could talk with vivacity, interest, knowledge, fluency and conviction about almost every conceivable subject. The way in which he was generally regarded as having universal knowledge and experience may be illustrated by the following true story. Some men were discussing the question of the weight of a horse, a subject on which they were not well informed, when one of them said: "Here comes Jackson. He knows everything. Let's ask him." When Jackson started his reply with the words: "When I last weighed a horse—" they all burst into laughter. That Jackson would have some reliable information about the weights of horses they had taken for granted, but that it should be of so direct and first hand a nature as his words implied seemed incredible. The writer, however, has little doubt that Jackson had weighed a horse and on more than one occasion.

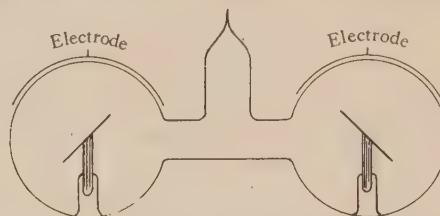
Jackson was a Fellow of the Institute of Chemistry, an institution in connexion with which he was very active, as Examiner, over periods totalling 8 years, as a Member of Council from 1904 to 1907, as a Vice-President from 1907 to 1908, 1916 to 1918 and 1921 to 1924, as a Censor from 1918 to 1935 and as President from 1918 to 1921. He was a Fellow of the Chemical Society and, for a period, a member of its Council.

To the various honours, dignities, public offices and positions otherwise important he received or occupied, which have already been mentioned in this notice, the following list may be added. He was a Fellow of the Physical Society (elected 1916), a Fellow of the Institute of Physics, an Honorary Fellow of the Royal Microscopical Society, an Honorary Member of the British Institute of Radiology, the President of the Röntgen Society from 1901 to 1903, a Vice-President and Member of Council of the Royal Society of Arts, a member of the Interdepartmental Scientific and Technical Committee on Optical Glass, and Chairman or a member of several committees connected with the Department of Scientific and Industrial Research, including the Adhesives Committee, the Stone Preservation Committee and the Building Research Advisory Committee. He was a member of the Advisory Committee on Scientific Research of the London, Midland and Scottish Railway and of other Committees of similar importance. He was a Member of the Senate of the University of London for a period of some years, a Governor of the Imperial College of Science and Technology, and the Chairman of the Technical Optics Committee of the Imperial College. He became a Member of the Royal Institution in 1924 and was a Manager of the Institution from 1930 to 1932 and from 1934 to 1935. He was elected a member of the Athenaeum in 1914 and took an active interest in the club and its affairs throughout the rest of his life.

Although he was a master of so many different branches of knowledge Jackson was by profession a chemist. As an illustration of the effect of his contact with his professional brethren and of some other matters the writer wishes to quote a passage from a notice in *The Analyst*, already referred to. It was written by one of his early students at King's College, R. B. Pilcher, Registrar and Secretary of the Institute of Chemistry, who is more familiar than the writer with this side of his activities. The passage is as follows: "If he did not achieve the reputation of a distinguished

chemist so soon as he deserved it was due to his dislike of putting pen to paper, although he was ever ready to impart his findings to his colleagues and students. Indeed, fellow chemists and others were often indebted to his inventive genius for original ideas, in the solution of problems and in devising chemical and physical apparatus, for which he received no material advantage and little or no credit.... Those who have worked with him have remarked that, at times, he seemed to possess imagination or intuition which enabled him to foretell results with almost uncanny accuracy. Indeed, when a research worker suggested a problem he would very likely be informed by Professor Jackson that he himself had already worked on it and had obtained certain results. This was a little disconcerting, perhaps, and it was sometimes thought that he had deceived himself, or was merely surmising, but he was invariably right as to the results."

In the early days of X rays Jackson constructed and experimented with X-ray tubes of almost every conceivable kind. He made one with external electrodes that worked. The construction and mode of operation of this tube will be clearer by reference to the figure. The glass envelope consisted of two spheres about 5 cm. in diameter joined by a straight tube about 4 cm. long and about 1 cm. wide or a little more, so as to form a symmetrical structure like a dumb-bell. The external electrodes were spherical metal caps of thin sheet extending to about a third of a hemisphere, and of the same curvature as the outer surface of the glass sphere to



which they were applied. The straight connecting tube had a side tube joining it at right angles in the middle, the whole forming a T-piece. This was initially connected to the pumps and afterwards sealed off. The external electrodes fitted the spheres and were applied as shown in the figure. The anticathodes thus generated X rays in cones having their axes either close to or roughly parallel to the axis of the connecting tube, and the whole structure was symmetrical about a plane perpendicular to this axis and containing the axis of the side tube. This tube gave X rays when the internal pressure was comparatively high, and the sharpness and symmetry of the focus depended on the centering and sphericity of the bulb, or of the part covered by the external electrodes. The X rays came from the target opposite to the electrode which was connected to the positive side of the induction coil.

The writer of the notice is indebted to Dr H. Moore for the following account of the way in which this very unusual X-ray tube probably functions. As the external electrodes become charged, the positive ions in the gas inside the tube are attracted to, and collect on, the inner surface of the glass beneath the negatively charged

electrode, while the negative ions and any electrons are attracted to the inner surface of the glass beneath the positive electrode. As soon as the surge from the induction coil is over, the external electrodes lose their respective charges, since they are connected to the secondary terminals of the induction coil, and are either completely discharged, or may become weakly charged, possibly in the reverse direction owing to the discharge through the induction coil being of an oscillatory character. The charges on the inner surfaces of the glass beneath the electrodes will then find themselves in an unstable condition, and will begin to disperse. From the negatively charged surface, the first units to escape will be the negative electrons, and they will escape while there is a strong accelerating field due to the negative ions distributed over, or still within a very small distance of the surface. The electrons will thus acquire comparatively high velocities immediately after the positively charged external electrode becomes discharged and, in striking the centrally mounted target, will emit X rays of appreciable penetrating power. The pressure in this tube was much higher than that of an ordinary X-ray vacuum, so high that in an ordinary discharge tube the electrons would have been caught by positive ions or gas molecules before they had travelled across to the target. It is probable that their traversing this path without being stopped is due to the facts that they would not be deflected very much by neutral molecules owing to their high speeds and also that there would be very few positive ions left in that part of the tube.

Jackson's famous focusing X-ray tube was a revolutionary improvement on all its predecessors. All of them gave beams of X rays coming from large and for the most part ill-defined and badly controlled areas. None of them could produce anything which could reasonably be called a picture. Jackson refused to patent his invention, a denial which should be remembered with gratitude by the public. It is said that had he done so he would have had a master patent covering all subsequent X-ray tubes. This is a matter of opinion or conjecture; but it is a fact of history that, although Jackson published his focusing X-ray tube in 1896 and demonstrated its capabilities at a Royal Society Conversazione in the same year, it was not until 1913, when Coolidge's thermionic cathode tube made its appearance, that any subsequent improvement, possessing both useful and practical importance as well as novelty, in the art of constructing X-ray tubes occurred. It is possible to regard Wehnelt's X-ray tube with a hot lime cathode (about 1905) as an anticipation of Coolidge's invention. It is probably as close an anticipation as could have been constructed and made to work with the materials available at the time; but it does not seem to have been of much use as a commercial or practical X-ray tube.

Whatever Jackson may or may not have done, he was the first to obtain an approximately point source of X rays and the first to construct an apparatus which produced anything which could now reasonably be called an X-ray picture, and he was the first human being to observe such a picture. Moreover, he did all this within a few weeks or at most a few months of Röntgen's announcement of his discovery. This accomplishment was no accident. It was the result of Jackson's particular and unusual combination of talents. These included a profound physical and practical insight into optics, unrivalled skill in the arts of constructing and

experimenting with vacuum electric discharge tubes and a wide and practical knowledge of phosphorescence and of phosphorescent substances and materials, together with a mastery of the photographic arts, all these being combined with great energy and unbounded enthusiasm for experimenting.

In 1900 he married Amy, the eldest daughter of the late Mr James Collister, a lady of great charm who survives him. Herbert Jackson was a glowing personality, a fine friend and a delightful companion. He was generous to a fault, both with gifts and hospitality, and also in helping those who worked with him, or under him, or who were associated with him as colleagues, as well as those who came to consult him about the many matters of which he was a master or on which he was a recognized authority. He was a man of happy disposition, kind-hearted and public-spirited. He will long be gratefully remembered by a wide circle of friends, former colleagues and old students and, indeed, by a host of people of all sorts with whom his very varied activities brought him into contact.

O. W. RICHARDSON.

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THE VARIATION OF VOLTAGE-DISTRIBUTION AND OF ELECTRON TRANSIT TIME IN THE SPACE-CHARGE-LIMITED PLANAR DIODE

BY R. COCKBURN, M.Sc., A.INST.P., West Ham Municipal College

Proc. Phys. Soc. **50**, 298 (1938).

DISCUSSION

Mr W. E. BENHAM. The author's analysis supplies in a most desirable form the static basis on which dynamic investigations of valve action must depend. As he indicates in his opening paragraph, the static transit time is of paramount importance. I would add that, even when the signal voltage is large, a knowledge of the static transit time is still required. Conversely, however small the signal, variations in electron transit time from the static value are of importance. There is a close connexion between the variation time and the electron convection current, and this connexion is particularly valuable in the temperature-limited condition (see, for example, reference 2 of the paper). The large percentage of time occupied by outgoing electrons between cathode and potential-minimum is likely to lead to complications when alternating voltages of high frequency are present. At low frequencies, where variations from the static transit time are of less importance, alternating current is derived only from a small range of initial velocities. Thus,

consider a triode with one volt alternating at the grid plane; let the height of the potential-minimum change by 5 millivolts between peaks as a result. Then, if V_0 represents the energy in electron-volts which an electron must have at the cathode in order to succeed in just passing the minimum with no signal,

$$(V_0 - 2 \cdot 5 \cdot 10^{-3}) - (V_0 + 2 \cdot 5 \cdot 10^{-3})$$

represents the range of initial velocities which, at very low frequencies, alone contribute to alternating anode current. The electrons which are of velocity greater than $(V_0 + 0 \cdot 0025)$ will pass whether there is alternating voltage or no, and are thus, except at high frequencies, no better than saturation current in a temperature-limited condition. It is sound to design sensitive valves to work under conditions for which V_0 is the most probable emission velocity, though in coated-cathode valves this would tend to be prejudicial to life.

I would take this opportunity of mentioning that the analysis of § 4·4, reference 10 of the paper, now appears to me to be inapplicable to the case worked out on pp. 24 and 25, so that equation (91) and parts of tables 1 and 4 are wrong.

In regard to applications it may be mentioned that in high-frequency screened-grid and pentode valves the input and output impedances depend, inter alia, on a knowledge of electron transit times in the various spaces concerned. As an application of rather wider scope may be mentioned the fact that if electron essential effects are correctly included, the dispersion of electromagnetic waves can be explained without recourse to frictional terms.

Mr D. M. TOMBS. The theory as outlined in the paper calls for as much as 25 per cent increase in transit time due to traverse from cathode to potential-minimum. J. Müller, in experiments on planar diodes, showed a close agreement between his results and his theory in which no allowance was made for transit from cathode to potential-minimum. Has the author been able to compare his results in this connexion with Müller's, or to make experiments himself?

AUTHOR'S REPLY. In reply to Mr Tombs: While it is true that the transit time between cathode and potential-minimum can be quite a large fraction of the total cathode-anode transit time, it does not follow that the total transit time is increased by this amount, since there is at the same time a reduction in the transit time between potential-minimum and anode. Thus, as is shown in figure 6, the total transit time may not be greatly different from the value for zero initial velocity used by Müller (*Hochfrequenztech. u. Electroakust.* **43**, 6, 195).

In considering Müller's results it should be noted that no allowance has been made either for initial velocities or for the large variation of transit time which can occur as the diode becomes space-change saturated.

I have not yet had an opportunity of verifying his results experimentally with a plane diode.

REVIEWS OF BOOKS

Thermodynamics, by E. FERMI. Pp. x + 160. (London: Blackie & Son.) 12s. 6d.

Each generation of teachers no doubt tries to avoid the errors of its immediate fore-runners, which of course it feels well qualified to judge since it suffered from them itself. We have just passed through a period when formal instruction in thermodynamics was reduced to a minimum, and a sign that we have entered the next phase is the rapid increase in the number of text-books on the market. This one does not fall below the standard that we should expect from its author, and those who have heard him speak either English or German will not be surprised to learn that it is written with a better sense of style than several which have recently appeared.

The scope is roughly that of other physics texts on thermodynamics; not that of engineering texts nor that of physical chemistry books, nor yet that of the books written for the out-and-out mathematician. It opens with chapters on the first and second laws (which are not treated in so much detail, either philosophically or historically, as in some other recent books) and proceeds to entropy and the thermodynamic potentials. Further chapters deal with gaseous reactions and dilute solutions respectively, and as an indication that they do not wander afield, we may note that neither "activity" nor "fugacity" occurs in the index. The last chapter, which deals with Nernst's theorem and the entropy constant, shows Fermi's originality more distinctly than the earlier ones.

Whilst the book is mainly concerned with fundamentals, it does not overlook the need for practice in details, and exercises are appended to each chapter; one of those from the final chapter may serve to indicate both the scope of the work and the standard of student for whom it is intended. Problem: "Calculate the degree of dissociation of sodium vapour at a temperature of 4000° K. and a pressure of 1 cm. of mercury. (Take into account not only the pressure due to the sodium atoms, but also the contribution of the ions and the electrons.)"

J. H. A.

The Fundamental Principles of Quantum Mechanics, by E. C. KEMBLE. Pp. xviii + 611. (McGraw-Hill Publishing Co., Ltd.) 36s. net.

This volume is a recent addition to the International Series on Physics. The form and appearance of these publications are so familiar to physicists that it is only necessary to state that this particular book contains 600 pages in order to indicate its size and comprehensive character. Its purpose and scope will be realized from the author's remark in the preface, that he has been influenced by the desire to meet the needs of graduate students of physics. A chapter has been included on the mathematical background of the theory in order to make the work to some extent self-contained. To give a complete idea of the contents it would be necessary to make a list of the headings of the chapters which are in many cases without any very obvious connexion with one another, so that the book is of the nature of a series of sections on the quantum theory. It is one of the most comprehensive works of reference on the subject and there appears to be no work except Frenkel's *Wave Mechanics* of a similar character.

There are chapters on Schroedinger's theory, on operator and matrix theory, on perturbations and on statistics, to choose only a few. Perhaps the outstanding feature of the work is the care in presentation of the subject which has resulted from the author's desire to be accurate. He has made the attempt to provide a bridge between the difficulties of the exact mathematical technique and the inaccuracies of some of the easy presentations of the subject. The author has without doubt a fine aesthetic physical and mathematical

sense, but, alas, he has not allowed this side of his character full play in the choice of notation. One is put off in glancing through the pages by the symbols with arrays of suffixes, crosses and stars that look like disfigurements. Is there any real need to speak of an operator $T^{(q)}$ or the unit operator $\alpha^{(x)}$? Shorthand can be carried too far, and it is continually necessary to turn back in the search for the meaning of the symbols, and to make matters worse in one place an operator is represented by two symbols.

The author claims to have added new material or to have made a departure in almost every chapter. But one wonders if this is an advantage. Its effect in the present case is to give the impression that he feared he might leave something out. He is not the only writer on quantum theory who seems to err in this respect.

The new quantum theory has now had a life equal to that of the Bohr theory, if we assign to the latter the years 1913-25, and we ought to begin to decide on an accepted mode of presentation combined with an accepted notation. With regard to the latter question we may remind ourselves that very little in the way of new notation has been required in the quantum theory. Mathematicians with true altruism discovered most of the notation necessary, never caring whether it would be useful to physicists or not. Their work might well be copied. It is still difficult to decide on a uniform mode of presentation of the subject because the theory is still growing, though the fundamentals are now largely established. Perhaps the difficulty arises from the attempt to write a book on quantum mechanics; one might almost equally well write on classical physics, so wide has the subject become.

Some of these remarks are not a criticism of the work under review in particular, they have their origin in the numerous publications that continually appear on modern physics and which it is difficult to read because of the variety of notations. There is no doubt that the present volume on account of its careful, complete and exact presentation of the subject is rightly described as a standard work.

H. T. F.

Elementary Physical Chemistry, by HUGH S. TAYLOR and H. AUSTIN TAYLOR.

Pp. xiii + 664. (Macmillan & Co.) 16s.

The first edition of this book appeared 10 years ago; since that time much work has been carried out on problems of atomic and molecular structure and their bearing upon the general field of reaction kinetics. The authors in their discussion of the gaseous state of aggregation introduce the concepts of collision-frequency and of varying velocity of gas molecules, and for this procedure there is a very good reason. In chemical reactions these are factors of prime importance. The study of velocity in gas reactions and the concepts of activation by collision and of gas reactions occurring at surfaces follow. These lead on to a discussion of the second law of energetics and the problem of equilibrium. The authors are to be congratulated on their clear exposition of these aspects of physical chemistry. The classical field of physical chemistry, that of electrolytes, is sub-divided under the headings of weak and strong electrolytes, and an introduction to the thermodynamic treatment of solutions is given. The physicist will study with interest the section devoted to methods for the determination of the charge on the electron, which includes a reference to the work of Birge and McMillan published in 1935 but omits work subsequent to that paper but published in 1935 and 1936. Lawrence's cyclotron is described. Of borderline subjects we are given an account of the work on Langmuir and others on the orientation of molecules, leading on to the more recent work of Rideal on chemical reactions occurring in monolayers. Specialists will inevitably find some omissions when an attempt is made to cover so wide a field: for example, no reference appears as to Kneser's work on the time of relaxation of molecules in collision. In this discussion of the atomic heats of metals the authors' brief account tends to give the impression that the Debye

formula fits the results with accuracy. Actually it does not do so, as was shown by Griffiths in the *Philosophical Transactions*, 1914.

The volume will be of great service to both physicists and chemists and the authors are to be congratulated on carrying through a valuable piece of work.

E. G.

Trigonometry, by T. M. MACROBERT and W. ARTHUR. Part III. *Advanced Trigonometry*. Pp. xi+134. 4s. 6d. Part IV, *Spherical Trigonometry*. Pp. x+61. 3s. (London: Methuen & Co.)

An earlier part of this new trigonometry has already been reviewed in these *Proceedings*, and as regards part III, it only remains to add that it follows directly on from the earlier volumes. It deals with the properties of sequences and series, somewhat on the lines of the treatment given in the senior author's *Complex Variable*.

Part IV, one of the few books in English on spherical trigonometry, will be bought by many readers who are not interested in the other parts. It deals only with the fundamentals: the properties of spherical triangles and their polars, the circumcircle and the incircle on a spherical surface, and the solution of spherical triangles. Two whole sections are devoted to the numerical solution of spherical triangles, the work being arranged for the use of logarithms, and to the reviewer it seems regrettable that the haversine method is ignored. This method, used by navigators (where speed is important) and in the Nautical Almanac Office (where accuracy takes precedence of other things) would not be worth teaching to the ordinary student if it required special apparatus or tables. But the formulae are particularly easy to remember, and tables of haversines and log haversines are easily available in Inman's nautical tables or Hall's four-figure tables (Cambridge). For those who are not familiar with it, we may say that

$$\text{hav } A [= \text{half versine } A] = \frac{1}{2} (1 - \cos A) = \sin^2 \frac{1}{2}A,$$

so that $\log \text{hav } A = 2 \log \sin (\frac{1}{2}A)$. Apart from this criticism, which in any case is a matter of opinion, the book is thorough and helpful, and is to be warmly recommended.

J. H. A.

Annual Tables of Constants and Numerical Data. Index to Volumes VI to X (Years 1923 to 1930). Pp. xxiv+352. (Paris: Hermann et Cie, 1937.)

This index is similar in conception to the earlier one, covering volumes I to V. It consists of two parts, the first an alphabetical index to properties and materials with common names. This part is in French, but the English, Italian and German names are entered in alphabetical position, with cross-references to the French names, when necessary. The second and longer part is a classification of compounds according to their formulae. Under each formula are given the properties for which values occur, together with the volume number and page. It will facilitate enormously the task of ascertaining whether data on a given compound are available in the volumes to which it refers.

J. H. A.

Tables Annuelles Internationales de Constantes. Vol. XI, 1st Part. Pp. xxii+493. (Paris: Hermann et Cie, 1937.)

Several times in the history of the Annual Tables a serious lag has grown up between the date of publication and the date of recording of data. At the moment, all data subsequent to 1930 require collection. The data up to 1936 will be included in two volumes, nos. XI and XII, each of which will be divided into three parts, though the six parts will only make four books, viz. vol. XI, part 1; vol. XII, part 1; vols. XI and XII, part 2; and vols. XI and XII, part 3. In addition, two sections of vol. XI appear only as monographs.

The part before us is part I of the eleventh volume, and covers the years 1931 to 1934. It is printed on a smaller page than that used for previous volumes and on better paper, so that it is now very pleasant to handle and to read. Its first 350 pages are mainly occupied with general physics and heat (acoustics is included, with seven pages) followed by electrical conduction, magnetism, and the minor electrical effects. An interesting opening is a section on universal constants, in which e is given as $(4.805 \pm 0.005) \times 10^{-10}$ e.s.u., \hbar as $(6.62 \pm 0.01) \times 10^{-27}$, $1/\alpha$ as 136.8 ± 0.3 and the absolute zero of temperature as $-273.19 \pm 0.03^\circ\text{C}$.

As far as it has been possible to verify, the editors have spread a fine-meshed net widely, and have missed very little. As usual, the main text is in French, generally duplicated in English, whilst the introductory matter is also given in German (where Dichte and Zähigkeit are interchanged on page vi) and Italian. The subjects for which we must wait until parts 2 and 3 are optics, atomic physics, physical chemistry and metallurgy, though some sections from these have already been completed and have appeared in monograph form. An index to all the parts of volumes XI and XII is promised in due course, similar to the index to volumes VI to X, which receives notice elsewhere in this issue.

J. H. A.

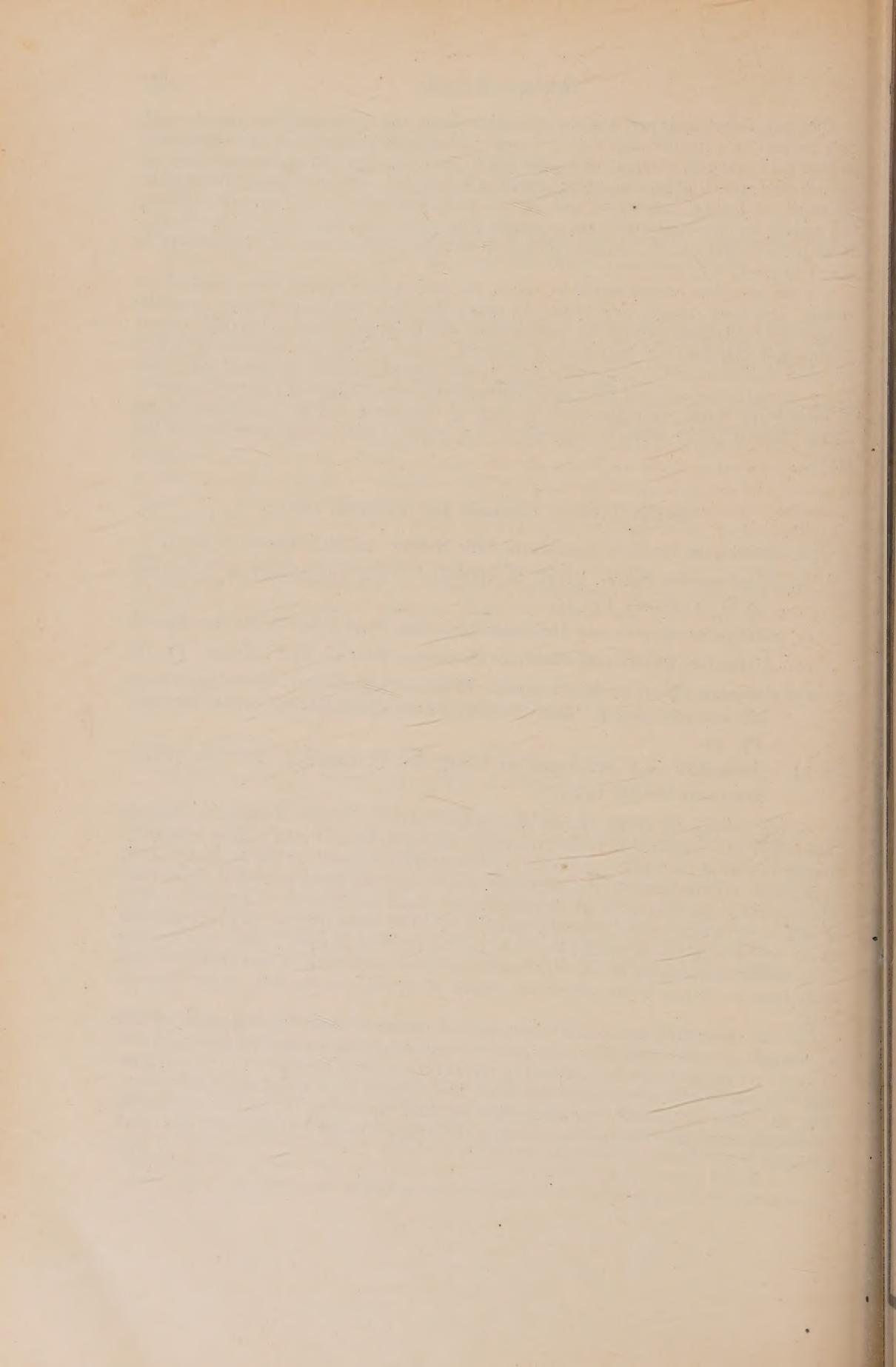
Annual Tables of Constants and Numerical Data

1. *Deuterium*, by G. CHAMPETIER, Mlle BONNET and M. MAGAT. Pp. 78.
9. *Electromotive Forces*, by H. S. HARRED. Oxidation-Reduction Potentials, by G. ÅKERLÖF. Pp. 45.
11. *Molecular Spectra and Molecular Structure*. Part I, by V. HENRI. Pp. 96.
12. *Molecular Spectra and Molecular Structure*. Part II, by V. HENRI. Pp. 66.
13. *Paraday Effect*, by M. SCHÉRER. Magnetic and Electric Birefringence, by A. COTTON and J. RABINOVITCH; Photo-electricity by G. A. BOUTRY. Pp. 40.
14. *Combustion and Detonation of Gases*, By P. LAFITTE. Pp. 28. (Paris: Hermann et Cie, 1937.)

As was announced in the preface of a recent volume of *Tables Annuelles de Données Numériques*, it is intended in future to sell the various sections of each volume separately, though of course the whole volume can still be obtained bound. It will be noticed that, to facilitate this arrangement, the pagination now commences afresh in each of the sections or subsections, the number of which precedes the actual page number. Thus 70-9 is p. 9 of section 70 (which occurs in monograph No. 14). The literature covered by the sections under review is not all of exactly the same period, but it is all quite recent. The sections form useful supplements to any other tables and it is interesting to note that they tend more than in the past to cite references instead of copying out the data, where these are bulky.

To turn over the pages of the monograph on deuterium and its compounds (to take an example almost at random) is an impressive reminder of the rate at which measurements of very varying worth are being added to the world's stock of information, a rate so great that it is not surprising to find voices lifted from time to time urging us to slow down. The rate leads to the need for such tables as these, as well as for various abstracting periodicals; and then requires monographs and annual reports to help us to take stock periodically.

J. H. A.



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